Supporting Information

Material-selective doping of 2D TMDC through

$\text{Al}_x\text{O}_y$ encapsulation

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1. **In depth discussion on IPE/PC interpretation and parameter extraction**

IPE/PC measures the current generated by the drift of photoexcited electrons which are able to overcome specific barriers inside the structure. As the photon energy increases, the electrons are able to overcome larger and larger barriers. In this technique, spectral analysis is commonly done with the $Y^{1/2} \cdot h\nu$ (Fowler) plot, by fitting the linear parts of the curves, and extrapolating to the background level of the measured current. The intersection between this linear fit and the background level gives the given barrier. We repeat the blue curve of figure 6 of the paper here for clarity.

![Figure S1](image_url) **Figure S1** IPE quantum yield as a function of photon energy $h\nu$ plotted in $Y^{1/2} \cdot h\nu$ (Fowler) coordinates, for the case where 12 V are applied on the top electrode, and electrons are injected from the Si substrate.

So, we would like to start by looking at the two most clear photocurrent thresholds, the $Al_xO_y$ bandgap (transition number 4 in inset schematic) and the one between the valence band of Si and the conduction band of $Al_xO_y$ (number 1 in inset schematic). When looking at number 4, the PC of $Al_xO_y$, it can be seen that we fitted the linear part of the curve above 6 eV and extrapolated it to a yield$^{1/2}$ of zero. This intersection is $\approx 6$ eV, which means that the bandgap ALD $Al_xO_y$ deposited on Si is $\approx 6$ eV. This means that the electrons from the valence band of $Al_xO_y$ are excited to the conduction band when absorbing a photon with energy of $\approx 6$ eV or larger. When looking at the number 1 in the blue curve, the IPE from the valence band of Si into the conduction band of $Al_xO_y$, it can again be seen that we fitted the linear part of the blue curve and extrapolated to a yield$^{1/2}$ of zero. In this case, the electrons which absorb photons with $h\nu > 3$ eV are able to surpass this Si/ $Al_xO_y$ barrier. This means that the valence band of silicon is located $\approx 3$ eV below the conduction band of $Al_xO_y$.

When looking at the grey curve (repeated below for clarity), however, the electron injection occurs from the Al pad, not from the Si layer. This happens because the MOS structure is biased with opposite voltage, so the bands bend the opposite way preventing electron drift from Si photoemitter into the oxide. The last transition, number 4 (PC of $Al_xO_y$), is still the same, since it is after all the same structure, and the electrons from the valence band of $Al_xO_y$ can still be excited to its own conduction band when photons above 6 eV are irradiated in the sample. Transition number one is now coming from electrons being excited from the occupied states in the metallic aluminum pad to the conduction band of $Al_xO_y$. The barrier is calculated by fitting the linear part of the curve and extrapolating, and we get a value of
≈2.8 eV, which means that the highest filled state close to the Fermi level of Al lies 2.8 eV lower than the conduction band of Al$_x$O$_y$, in good agreement with previous results$^1$.

Now we turn our attention to the two defect bands inside the oxide, first looking at the case that electrons are injected from the Al pad (grey curve). Since they both occur at an energy higher than the first transition and lower than the last, they are located (in energy) between 2.88 eV below the conduction band of Al$_x$O$_y$ and the edge of the conduction band. The fact that these same two defect signatures occur in the two polarities tells us that they are not coming from either electrode (Al or Si), but the source of electrons is spatially inside the oxide layer.

Finally, we would like to evaluate the slope of the curves obtained in both polarities, to further support our argument that the two yield peaks, which we attribute to defect bands, are indeed coming from the same source, which is independent on the structure polarity. For this we calculate the slope of each curve and normalize them (for simplified analysis). This graph is shown below. We see that as the photon energy increases, the slope starts increasing as well, with a distinct increase present in the blue curve (electrons injected from Si) which is not present in the grey (electrons excited from Al). This peak is the E$_1$ singularity of Si, which is referred in the main text as a “kink” in the curves.

Around 3.5eV, both curves follow a distinctively similar shape, with a first broad increase in the slope and then a strong dip in the curves. IPE/PC curves don’t commonly have negative slopes, because this means that electrons are absorbing energy from photons but not being excited to conduction band. Instead, electrons are being moved from a bonding π orbital to an antibonding π* orbital. These electrons do not contribute to the measured current, and thus a dip in the Yield$^{1/2}$(and Slope) is observed. Interestingly, this π – π* transition only occurs in the presence of π orbitals, which, in turn, are a signature of C=C molecular bonds. This is a direct observation of the presence of π orbitals inside the bandgap of Al$_x$O$_y$, in the relevant energy range to explain the n-type doping we observe.

The second defect band, in turn, can then be seen as the increase in slope from 4.5 eV to a maximum close to 5 eV, which indicates further defects deeper in the Al$_x$O$_y$ bandgap. The nature and position of
those defects are unknown to us at this moment, but since they are too deep, they are not the ones resulting in the doping we observe.

Figure S3 Normalized slope for the $Y^{1/2} \cdot h\nu$ (Fowler) IPE quantum yield as a function of photon energy $h\nu$ for both polarities, highlighting that the defect states and $\pi - \pi^*$ transitions are seen irrespective of the origin of the photoexcited electrons (Al or Si).
2. SEM and AFM images of devices

2.1 SEM of MOCVD MoS$_2$ and MOCVD WS$_2$

<table>
<thead>
<tr>
<th>Device</th>
<th>MOCVD MoS$_2$/Al$_x$O$_y$</th>
<th>MOCVD WS$_2$/Al$_x$O$_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Au contacts</td>
<td>Ni/Au contacts</td>
<td>Ni/Au contacts</td>
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<tr>
<td>Particles</td>
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<tr>
<td>Strain-induced</td>
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<tr>
<td>crack</td>
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Figure S4 SEM images of MOCVD MoS$_2$ and MOCVD WS$_2$ covered with ALD Al$_x$O$_y$. a,b) image of devices, showing metallic contacts and TMDC channel, both regions covered by a thick layer of Al$_x$O$_y$. c,d) image on a region far from devices, with TMDC is covered by thick Al$_x$O$_y$. From SEM images, ALD film appears closed.
2.2 AFM of MoS$_2$, WS$_2$, ReS$_2$ flakes in all stages of fabrication

<table>
<thead>
<tr>
<th>Upon exfoliation</th>
<th>After metal deposition</th>
<th>After Al$_2$O$_3$ deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="MoS$_2$ Flakes" /></td>
<td><img src="image2" alt="WS$_2$ Flakes" /></td>
<td><img src="image3" alt="ReS$_2$ Flakes" /></td>
</tr>
</tbody>
</table>

**Figure S5** AFM topography maps of MoS$_2$ (a, d, g), WS$_2$ (b, e, h), ReS$_2$ (c, f, i) flakes in different stages of fabrication. Thin flakes are identified and characterized after exfoliation (a, b, c), source and drain metal contacts are deposited on the flakes using e-beam lithography and metal lift-off (d, e, f) and ~30nm Al$_2$O$_3$ is deposited on top of the flake transisors (g, h, i). Electrical measurements are performed before and after Al$_2$O$_3$ deposition.
3. $I_{DS} \times V_{GS}$ curves of MoS$_2$ transistors covered with standard and underdosed Al$_x$O$_y$

![Graph showing $I_{DS} \times V_{GS}$ curves](image)

Figure S6 Representative $I_{DS} \times V_{GS}$ curves for short (a) and long (b) channel transistors with bare MoS$_2$, and after standard and underdosed ALD Al$_x$O$_y$.

Representative curves are shown for bare MoS$_2$, and after depositing standard and underdoses aluminum oxide. As discussed in the main text, reducing the dose of the oxidant precursors leads to stronger doping effect, with higher maximum currents and lower gate-modulation. Higher material defectivity in this case leads to lower currents than the ones shown in the main text. The trend, however, is repeatable for a large number of devices (14 to 23, depending on the condition).

4. X-Ray Reflectivity of standard and “underdosed” Al$_x$O$_y$

![Graph showing X-Ray Reflectivity](image)

Figure S7 X-Ray reflectivity of standard and underdosed Al$_x$O$_y$ on HF-cleaned Si, showing significant differences in terms of amplitude of vibration, the period of oscillation, and the vibration decay rate (related to density, thickness, roughness, etc.) between the films.

XRR measurements are done on ALD Al$_x$O$_y$ grown in two different manners, on HF-cleaned Si, our representative system. Measurements were done using XRD diffractometer X’pert with Pixcel 2.0 detector and Cu/NW mirror. The X-ray wavelength from the Cu KR X-ray tube was 1.54 Å. The electron beam current in the X-ray tube was 40 mA at 45 kV. A 2θΩ scan was performed with 10-arcsec step size and a 5 minutes total acquisition time.

The measurements show significant differences between the aluminum oxide deposited with standard parameters, and the one where an underdosing of the oxidant precursor (H$_2$O) is employed. It can be noted that the critical angle (related to film density) is similar for the two samples, but not exactly the same. Furthermore, the amplitude of vibration, the period of oscillation, and the vibration decay rate
are distinctly different in the two cases, highlighting the fact that by reducing the oxidizing precursor dose, we are able to produce oxides with distinct characteristics (density, thickness, roughness, etc).

5. XPS data of MoS$_2$ covered with standard and “underdosed” Al$_x$O$_y$

![Figure S8](image)

**Figure S8** Mo3d and S2p core levels of bare MOCVD MoS$_2$ and after covering with 20 cycles of standard and de-tuned Al$_x$O$_y$. By using few cycles, a very thin layer of Al$_x$O$_y$ is formed and the XPS can still probe the 2D material underneath. MoS$_2$ is negligibly degraded by the ALD process (no significant increase in peaks related to MoO$_3$ and SO$_4$), irrespective if the standard or non-standard parameters are used.

![Figure S9](image)

**Figure S9** C1s core level of bare MOCVD MoS$_2$ and after covering with 20 cycles of standard and de-tuned Al$_x$O$_y$. By using few cycles, a very thin layer of Al$_x$O$_y$ is formed and the XPS can still probe the 2D material underneath, but the presence of adventitious carbon (C-C, C-H) is strongly enhanced, compared to the partial milling shown in Figure 5b of the main text. O-C=O peak in bare MoS$_2$ shifts towards O-C-O or C-O peak, indicating a partial conversion or removal of the possible polymeric residues during the ALD process. The Al-C peak mentioned in the main text is not visible in these spectra, probably due to the strong signal coming from adventitious carbon (C-C, C-H), which is located closely to the Al-C peak.
6. Raman spectra of MoS$_2$, WS$_2$ and ReS$_2$ before and after ALD oxide deposition

Figure S10a,b show the Raman spectra of synthetic and flake MoS$_2$ layers, before and after oxide deposition. All spectra were acquired with 532nm (green) laser. Raman is a powerful tool, which can provide information in strain ($E_{2g}$ peak) and doping ($A_{1g}$ peak) of MoS$_2$. As it is clearly seen in the graphs, the $E_{2g}$ peak remains at the same position before and after oxide deposition, indicating that the 150 °C ALD process does not induce any observable strain in the layers. Strong doping is observed, however, from the broadening in softening of the $A_{1g}$ peak of both synthetic and flake MoS$_2$ after Al$_x$O$_y$ deposition.

When analyzing the Raman spectra of WS$_2$ flakes before and after Al$_x$O$_y$ (Figure S10b), one has to be more careful, due to the overlapping of the resonant 2LA peak. Nonetheless, it is apparent that the peak positions don’t significantly change in this case, indicating that neither strain nor doping are strongly different after the Al$_x$O$_y$ deposition, which agrees with the electrical results.

Raman spectra of ReS$_2$ is reproduced in Figure S10c to complete the dataset. In this case, the effect of doping or strain in the Raman peaks is not well established. Small differences in the two spectra can nonetheless be observed.

**Figure S10** Raman spectra of MoS$_2$ (synthetic and flakes), WS$_2$ and ReS$_2$ flakes, before and after ALD Al$_x$O$_y$ deposition. No sign of strain is observed in any case ($E_{2g}$ peak remains at the same position). Strong doping is seen on MoS$_2$, with softening and broadening of $A_{1g}$ peak. Doping signature has still not been established for Raman of ReS$_2$ layers.