Supporting Information

Growth of 2H Stacked WSe$_2$ Bilayers on Sapphire

Ali Han$^1$, Areej Aljarb$^1$, Sheng Liu$^2$, Peng Li$^1$, Chun Ma$^1$, Fei Xue$^1$, Sergei Lopatin$^3$, Chih-Wen Yang$^1$, Jing-Kai Huang.$^{1,4}$, Yi Wan$^1$, Xixiang Zhang$^1$, Kuo-Wei Huang$^1$, Qihua Xiong$^5$, Vincent Tung$^{1,6*}$, Thomas D. Anthopoulos$^{1*}$, Lain-Jong Li$^{1,4*}$

$^1$Physical Sciences and Engineering Division (PSE), King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia

$^2$Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371

$^3$King Abdullah University of Science and Technology (KAUST), Core Labs, Thuwal, 23955-6900, Kingdom of Saudi Arabia

$^4$School of Materials Science and Engineering, University of New South Wales, Sydney, NSW 2052, Australia.

$^5$Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371. MajuLab, CNRS-UNS-NUS-NTU International Joint Research Unit, UMI 3654, Singapore 639798. NOVITAS, Nanoelectronics Center of Excellence, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798

$^6$Molecular Foundry Division, Lawrence Berkeley National Lab, Berkeley 94720, USA

* E-mails: thomas.anthopoulos@kaust.edu.sa; vincent.tung@kaust.edu.sa; lance.li@kaust.edu.sa;
Figure S1. Schematic illustration of the CVD setup and the relative position between WO$_3$, Se and substrate. The distance between Se powder and WO$_3$ powder is ~25 cm.
Figure S2. Optical images for the WSe$_2$ growth by CVD method. The mass amount of WO$_3$ is 0.3g, while the amount of Se powder is increased. The high-purity of H$_2$/Ar is as the carrier gas with a fixed flow rate of 5/65 sccm/sccm. The T$_{Se}$ (temperature of Se) is maintained at 250 °C while T$_{WO_3}$ (the temperature of WO$_3$) is kept at 895 °C. The growth pressure of the furnace is 10 torr for the whole CVD growth. The growth time is 15 mins.
Figure S3. Optical images for the WSe$_2$ growth by CVD method. The mass amount of WO$_3$ is 0.3 g. The high-purity of H$_2$/Ar is as the carrier gas with a fixed flow rate of 5/65 sccm/sccm. a-b, The amount of Se powder is 5.5 g, $T_{\text{Se}} = 250$ °C and $T_{\text{WO}_3} = 890$ °C; c-d, The amount of Se powder is 5.0 g, $T_{\text{Se}} = 260$ °C and $T_{\text{WO}_3} = 895$ °C; e-f, The amount of Se powder is 5.5 g, $T_{\text{Se}} = 250$ °C and $T_{\text{WO}_3} = 900$ °C.
Figure S4. a, Left: optical micrograph of cloud bilayer WSe₂ crystal with monolayer WSe₂ as reference; Right: The corresponding SHG mapping intensity obtained by pixel-to-pixel spatial scanning on the crystals in Fig. S4a; b, The SH signal spectra of different layer number; c, Optical micrograph of irregular bilayer WSe₂ crystal with monolayer WSe₂ as reference; d, The corresponding SHG mapping intensity obtained by pixel-to-pixel spatial scanning on the crystals in Fig. S4c; e, The SH signal spectra of different layer number.
Figure S5. Low-frequency Raman spectra of bilayer WSe$_2$ crystals for 2H and 3R stacking configurations with different morphologies.

Figure S6 a, Low-magnification HAADF-STEM image of top-view bilayer WSe$_2$ sample; b-c, elemental mapping of the region (green frame) in Fig.a.
Figure S7. a, AFM topographic image of the monolayer WSe$_2$ grain boundary crystal with bilayer nuclei in the center area; b, The zoom-in AFM topographic image of area 1, indicative of initial WSe$_2$ bilayer nuclei aligned growth on the atomic steps. Scale bars: a, 2 µm; b, 100 nm.
Figure S8. a-b, AFM topographic images of monolayer WSe$_2$ crystal with bilayer nuclei in different areas. The inset height profile is ~0.8 nm, indicating a thickness of WSe$_2$ monolayer. The zoom-in AFM image in Fig. R1b shows WSe$_2$ bilayer nuclei initial growth on the atomic steps of sapphire; c-d, AFM topographic images of monolayer WSe$_2$ crystal with bilayer nuclei in different areas. The inset height profile is ~0.76 nm, indicating a thickness of WSe$_2$ monolayer. The zoom-in AFM image in Fig. R1d shows WSe$_2$ bilayer nuclei initial growth on the atomic steps of sapphire.
Figure S9. a, AFM topographic image of sapphire surface after high-temperature treatment (1050 °C in H₂/Ar for 15 mins); b, the corresponding cross-section height profile of the atomic steps along the vertical step direction in Fig. S7a; c, AFM topographic image of sapphire surface after high-temperature treatment (1050 °C in air for 60 mins); d, the corresponding cross-section height profile of the atomic steps along the vertical step direction in Fig. S7c. Scale bars: a, 100 nm; c, 100 nm.
Figure S10. a, AFM topographic image of one WSe$_2$ crystal. The inset height profile was ~0.8 nm, indicating a monolayer thickness; b, The zoom-in AFM image in Fig. S8a. And the image showed irregular atomic steps on bare sapphire surface without any pre-treatment. In contrast, the apparently periodic atomic steps were shown after covering monolayer WSe$_2$; c, The selected area for the roughness calculation of bare sapphire surface (300 nm x 300 nm); d, The selected area for the average roughness calculation of sapphire surface with monolayer WSe$_2$ covering (300 nm x 300 nm). Scale bars: a, 2 µm; b, 200 nm; c, 2 µm; d, 200 nm.
Figure S11. a, Optical micrograph of bilayer/trilayer WSe$_2$ crystals as-grown on c-plane sapphire substrate; b, The Raman spectra measurements for bilayer (red) and trilayer (orange) WSe$_2$ crystals.
Figure S12. AFM topographic images of three representative bilayer WSe$_2$ crystals as-grown on sapphire surface. a, The bilayer WSe$_2$ crystal with irregular morphology. The inset height profiles were both ~0.8 nm, indicating a bilayer thickness in the left part and a monolayer thickness in the right part of the WSe$_2$ crystal; b, The zoom-in AFM image showed the bilayer WSe$_2$ nuclei growth orientation following the atomic steps; c, the bilayer WSe$_2$ crystal with truncated triangle morphology. The inset height profile demonstrated a bilayer thickness of WSe$_2$ crystal; d, The zoom-in AFM image showed bilayer WSe$_2$ nuclei growth orientation following the atomic steps; e, The bilayer WSe$_2$ crystal with grain boundary. The inset height profile demonstrated a bilayer thickness of WSe$_2$; f, The zoom-in AFM image showed bilayer WSe$_2$ nuclei growth orientation following the atomic steps. Scale bars: a, 2 µm; b, 200 nm; c, 1 µm; d, 200 nm; e, 1 µm; f, 100 nm.
<table>
<thead>
<tr>
<th>WSe₂ crystals</th>
<th>Sapphire Roughness</th>
<th>Monolayer Roughness</th>
<th>Bilayer Roughness</th>
<th>Trilayer Roughness</th>
<th>Sapphire Roughness (1050 °C)¹</th>
<th>Sapphire Roughness (1050 °C)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sapphire (Fig. S7a)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.056 nm</td>
</tr>
<tr>
<td>Sapphire (Fig. S7c)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.060 nm</td>
</tr>
<tr>
<td>Crystal 1 (Fig. 2b)</td>
<td>-</td>
<td>0.070 nm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Crystal 2 (Fig. 2d)</td>
<td>0.109 nm</td>
<td>0.073 nm</td>
<td>0.068 nm</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Crystal 3 (Fig. 3b)</td>
<td>0.129 nm</td>
<td>0.094 nm</td>
<td>0.097 nm</td>
<td>0.076 nm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Crystal 4 (Fig. S8b)</td>
<td>0.148 nm</td>
<td>0.056 nm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Crystal 5 (Fig. S10b)</td>
<td>0.110 nm</td>
<td>0.077 nm</td>
<td>0.082 nm</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Crystal 6 (Fig. S10d)</td>
<td>0.125 nm</td>
<td>0.081 nm</td>
<td>0.073 nm</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Crystal 7 (Fig. S10f)</td>
<td>-</td>
<td>0.075 nm</td>
<td>0.086 nm</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

¹The as-supplied sapphire was annealed in the H₂/Ar for 15 mins;
²The as-supplied sapphire was annealed in the air for 60 mins.
Figure S13. **a.** The Raman spectra measurements for WSe\(_2\) monolayer and bilayer crystals before and after device fabrication on c-plane sapphire substrate; **b.** The PL spectra measurements for WSe\(_2\) monolayer and bilayer crystals before and after device fabrication on c-plane sapphire substrate.
Figure S14. a, $I_{ds}$ as a function of $V_g$ for monolayer device with two terminal. $I_{ds}$ as a function of $V_g$ for bilayer device with two terminal; b, $I_{ds}$ as a function of $V_g$ for monolayer device. $I_{ds}$ as a function of $V_g$ for bilayer device. $C_g = 5.0 \ \mu F/cm^2$; c, $I_{ds}$ as a function of $V_{gs}$ for monolayer/bilayer device. The subthreshold slopes of monolayer and bilayer crystals were measured to be 229 and 201 mV/dec, respectively.