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Supplementary Material

Covalent Nitrogen Doping in MBE and Bulk WSe_2

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Outline:

1. O 1*s* and C 1*s* core levels and Valence Band *Maximum* before and after annealing
2. Sequential N_2 plasma exposure
3. HOPG Substrate after N_2 plasma exposure
4. Angle resolved XPS (AR-XPS)
5. Surface structure of MBE WSe_2 after 30 min N_2 plasma exposure

O 1*s* and C 1*s* core levels and Valence Band Maximum before and after annealing:

Figures S1(a) and 1(b) show O 1*s* core level spectra obtained from both MBE-grown and bulk WSe_2 samples. A very low concentration of oxygen near the XPS detection limit is present on both samples due to the short (< 10 min.) air exposure prior to loading into UHV. Adventitious oxygen was removed from the surface by annealing in UHV at 300 °C for 2 hours. The C 1s core level spectra obtained from MBE and bulk WSe_2 before and after annealing (Figure S1(c-d)) are convoluted with a Se LMM Auger feature centered at ~284.3 eV. The intense chemical state detected at 284.4 eV in the C 1*s* core level obtained from MBE WSe_2 (Figure S1(c)) originates from the highly oriented pyrolytic graphite (HOPG) substrate used to grow MBE WSe_2. Adventitious carbon detected on exfoliated WSe_2 at 284.5 eV is presumably liberated during annealing as any residual carbon is below the limit of XPS detection in the corresponding C 1*s* spectrum (Figure S1(d)). Figure S1(e) and (f) shows the Valence Band Maximum before and after annealing in 300 °C for 2 hours for MBE grown WSe_2 and exfoliated WSe_2. VBM reveals no significant changes before and after annealing in both samples.

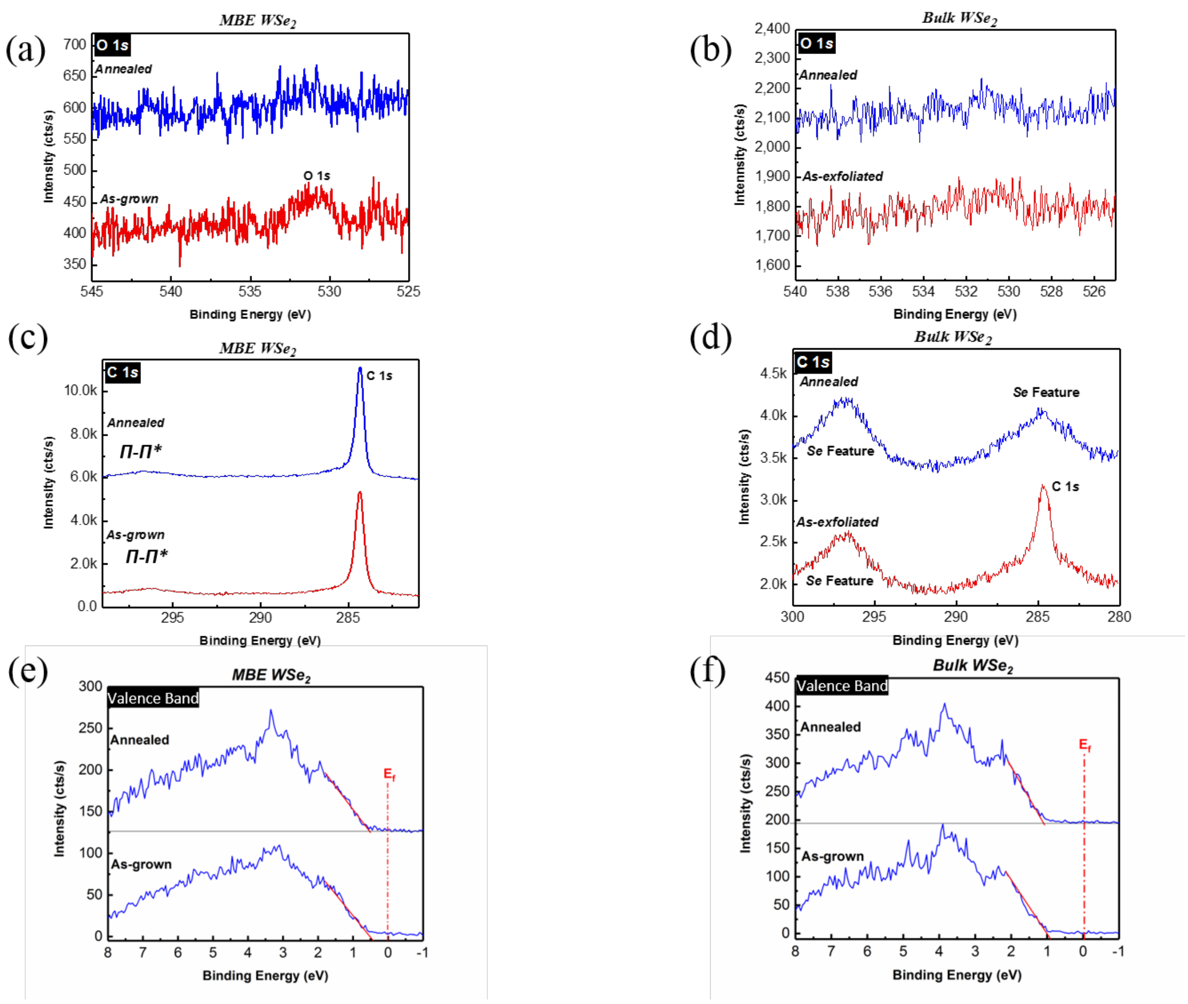

Figure S1: O 1*s* core level spectra obtained from (a) MBE WSe_2 and (b) Exfoliated WSe_2 before (red) and after (blue) annealing. C 1*s* core level spectra obtained from (c) MBE-grown WSe_2 and (d) exfoliated WSe_2 before (red) and after (blue) annealing. VBM of (e) MBE WSe_2 as-grown and after annealing (f) Exfoliated WSe_2 as-exfoliated and after annealing.

Sequential N_2 plasma exposure:

The results reported here show nitrogen concentration in the vicinity of the WSe_2 surface can be tuned by controlling the exposure time to the remote N_2 plasma. Figure S2 indicates the nitrogen incorporation into WSe_2 samples (MBE and bulk) increases as the N_2 plasma exposure time increases. In addition, evolution of x and y in WN_xSe_y (nitrogen plasma–treated WSe_2) for both MBE and bulk samples are shown in Figures S2(c) and 2(d).

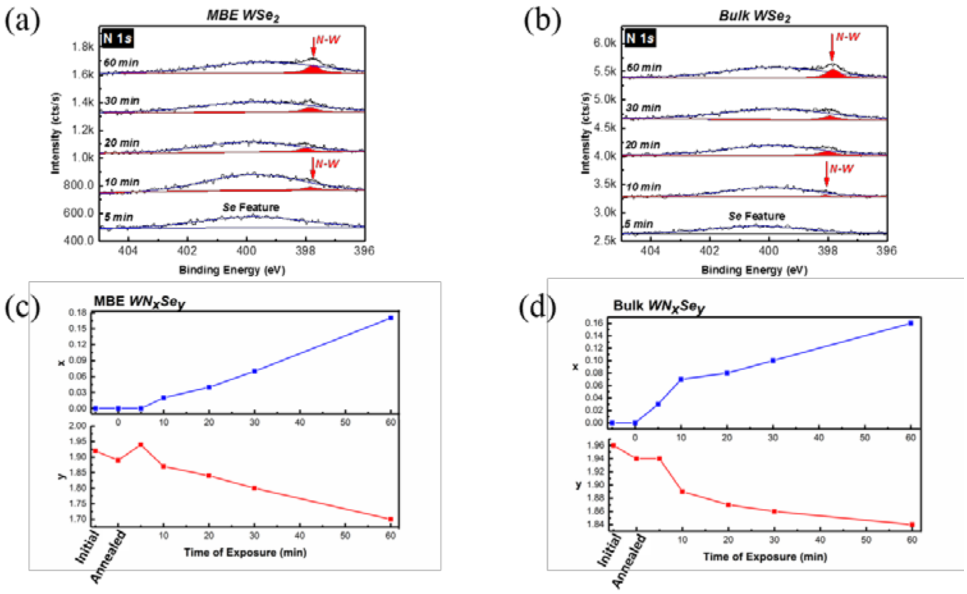

Figure S2: N 1*s* core level spectra obtained from (a) MBE-grown and (b) bulk WSe_2 after 5, 10, 20, 30, and 60 min N_2 plasma exposure. Stoichiometry of nitrogen plasma-treated WSe_2 presented as x and y in WN_xSe_y for (c) MBE-grown and (d) bulk initial, annealed, after 5, 10, 20, 30, and 60 min N_2 plasma exposure.

HOPG and SiO_2 substrate after N_2 plasma exposure:

Surface chemistry of substrate after N_2 plasma treatment has been studied. C 1*s* core level from HOPG substrate is shown before any treatment, annealed, after 30, and 60 min N_2 plasma exposure. These spectra demonstrate that there are not any significant changes on the substrates after the treatment. This is a solid evidence that treatment does not affect the substrate underneath.

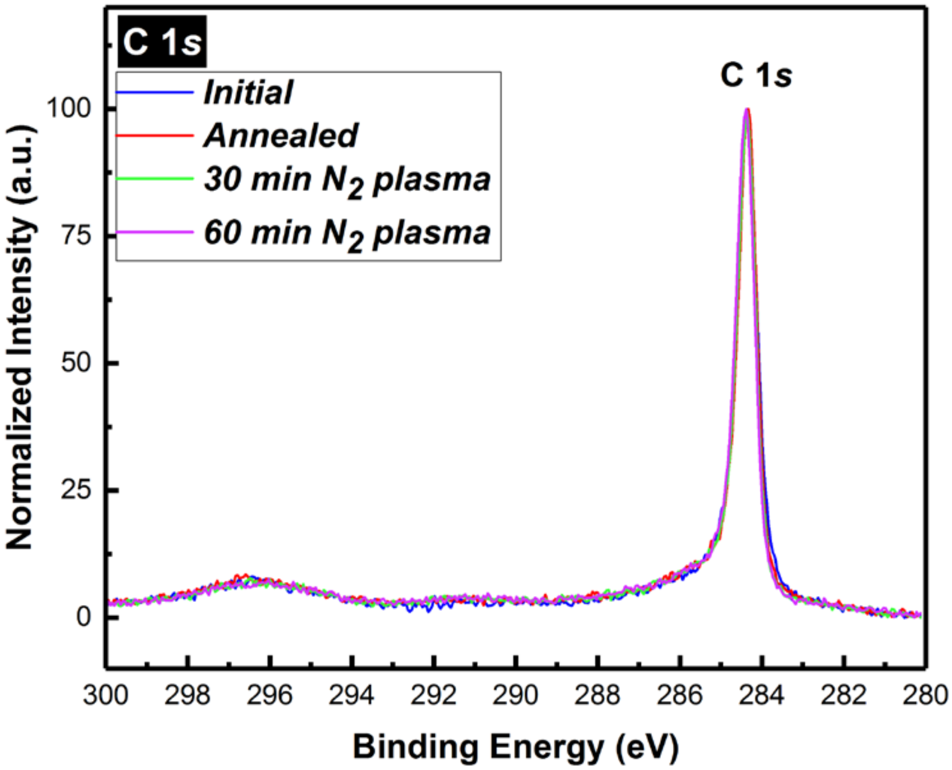

Figure S3: C 1*s* core level from HOPG substrate before any treatment, annealed, after 30, and 60 min N_2 plasma exposure

Angle Resolved XPS (ARXPS):

In an attempt to qualitatively determine the location of nitrogen atoms in treated WSe_2 samples relative to the surface, core level spectra were obtained from both MBE (Figure S3(a)) and bulk (Figure S3(b)) WSe_2 samples after 30 min plasma exposure at take–off angles of 45° and 75° (comparably more bulk sensitive than 45°). The N 1*s* core level obtained from the few-layer MBE WSe_2 film does not show significant spectral intensity changes as a function of take-off angle (Figure S3(a)). In contrast with the MBE WSe_2 surface, exfoliated WSe_2 (Figure

S3(b)) exhibits a clear reduction in the intensity of the corresponding N 1*s* core level with increased take-off angle, suggesting nitrogen is localized to the outermost WSe_2 layers.

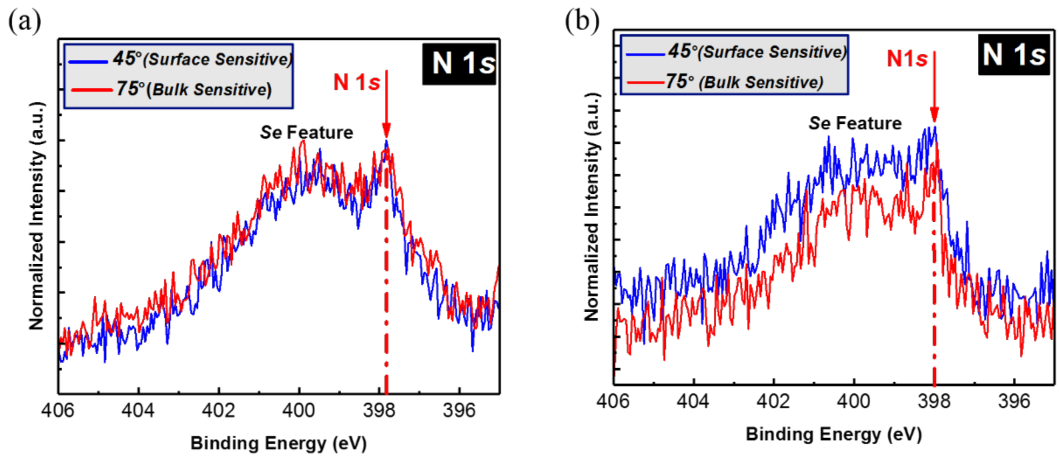

Figure S4: N 1*s* core level spectra obtained from (a) MBE WSe_2 and (b) exfoliated WSe_2 at takeoff angles of 45° (blue) and 75° (red) after 30 min plasma treatment.

Surface structure of MBE WSe_2 after 30 min N_2 plasma exposure:

STM images obtained from small size MBE WSe_2 domains suggests the N_2 plasma treatment employed in this work is destructive when applied to WSe_2. Specifically, damage is accentuated in smaller domains presumably due to their higher step edge–to–terrace ratio compared with larger domains. The STM image in Figure S4(a) shows the surface structure of bilayer WSe_2 before N_2 plasma treatment and Figure S4(b) exhibits WSe_2 domains following 30 min N_2 plasma treatment. The treatment causes a significant degradation of the WSe_2 surface and increase in the surface roughness from 0.4 nm to 1.6 nm (Figure S4(c) and 4(d)).

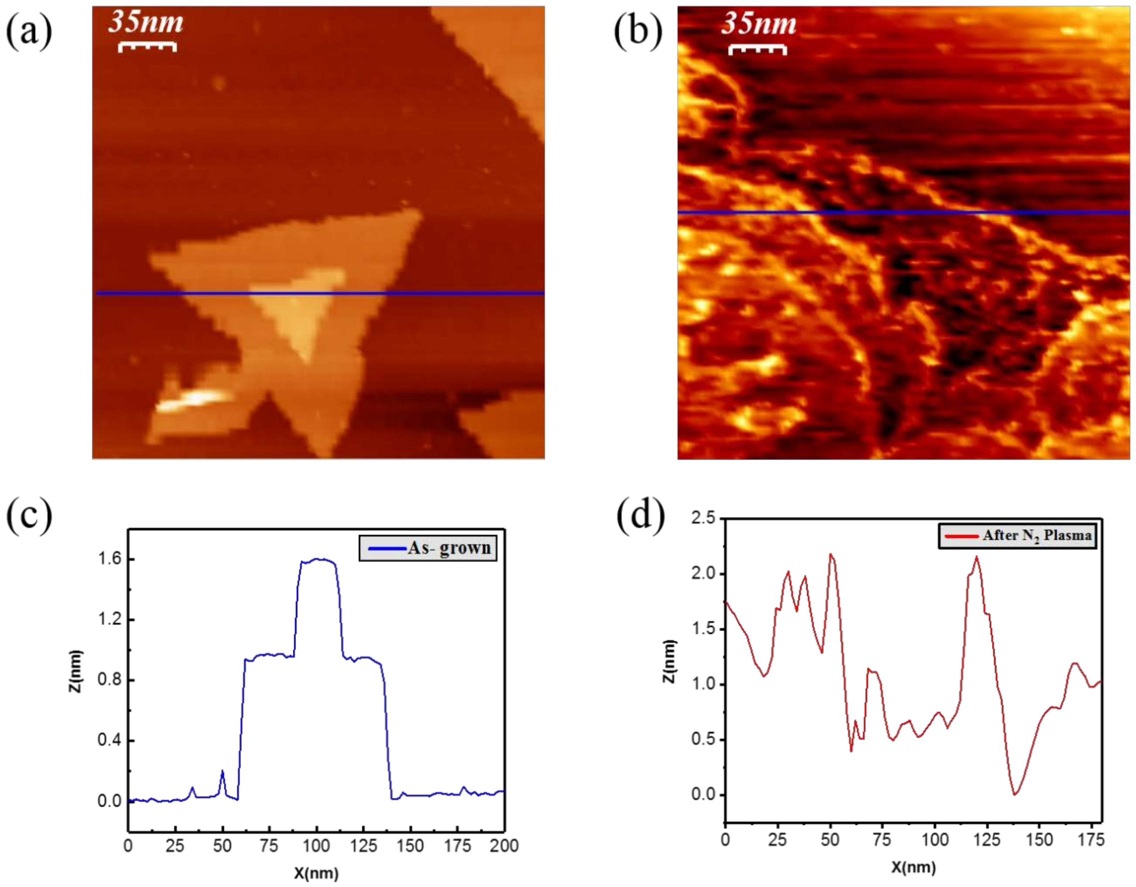

Figure S5: STM image of (a) bilayer MBE WSe_2 and (b) MBE WSe_2 after 30 min N_2 plasma exposure. Line profiles associated with (a) and (b) are shown in (c) and (d), respectively.