

Supporting Information

Controlling Catalyst Bulk Reservoir Effects for Monolayer Hexagonal Boron Nitride CVD

Sabina Caneva,¹ Robert S. Weatherup,^{1,2} Bernhard C. Bayer,^{1,3} Raoul Blume,⁴ Andrea Cabrero-Vilatela,¹ Philipp Braeuninger-Weimer,¹ Marie-Blandine Martin,¹ Ruizhi Wang,¹ Carsten Baehtz,⁵ Robert Schloegl,⁶ Jannik C. Meyer,³ and Stephan Hofmann^{1,}*

¹Department of Engineering, University of Cambridge, JJ Thomson Avenue, CB3 0FA, Cambridge, UK.

²Materials Sciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley CA 94720, USA.

³Faculty of Physics, University of Vienna, Boltzmanngasse 5, A-1090 Vienna, Austria.

⁴Helmholtz-Zentrum Berlin für Materialien und Energie, D-12489 Berlin, Germany.

⁵Institute of Radiation Physics, Helmholtz-Zentrum Dresden-Rossendorf, 01314 Dresden, Germany.

⁶Fritz Haber Institute, D-14195 Berlin-Dahlem, Germany.

*Corresponding Author: sh315@cam.ac.uk

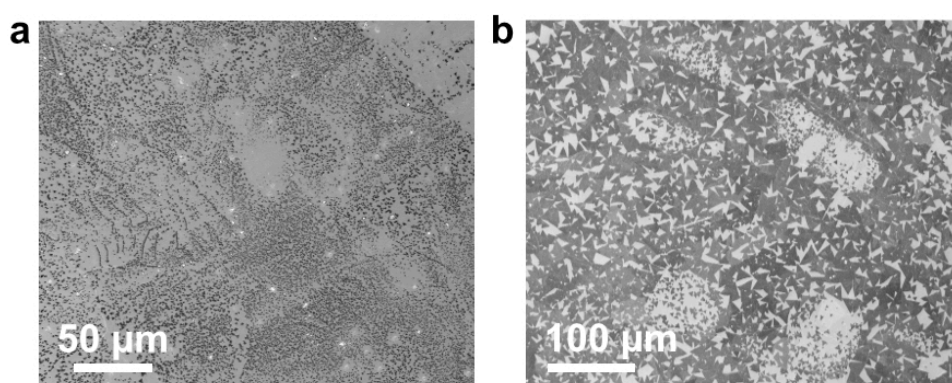


Figure S1. SEM image of h-BN domains grown at ~ 900 °C and 6×10^{-4} mbar borazine exposure for 60 s for (a) H₂-preannealed Fe foil and (b) NH₃-preannealed Fe foil. The images show that the h-BN domain density and size varies across the sample surface for both foils, indicating that preferential h-BN growth on certain Fe grains occurs for both preannealings.

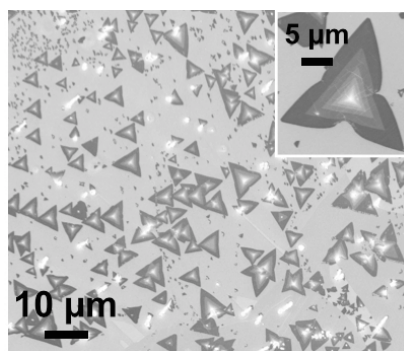


Figure S2. SEM image of bimodal h-BN size distribution [4 mbar H₂-preannealing, ~900 °C, 6×10^{-4} mbar, 5 min], with many small domains nucleated between the larger triangular domains. Inset: detail of a thick multilayer domain.

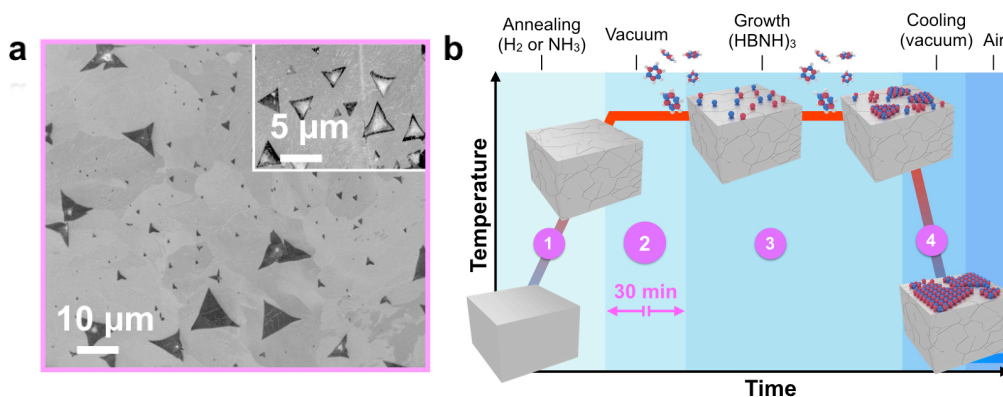


Figure S3. (a) SEM image of h-BN domains grown on NH₃-preannealed Fe foil after holding the sample 30 min in vacuum prior to borazine dosing. The growth was then carried out at ~900 °C and 6×10^{-4} mbar borazine exposure for 90 s. **(b)** Temperature profile illustrating the extended Stage 2, corresponding to this growth.

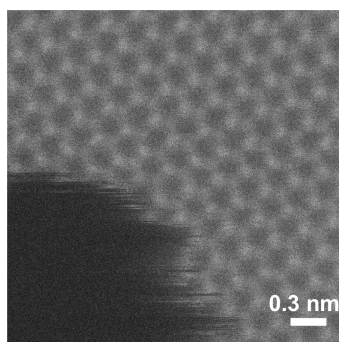


Figure S4. STEM image (unprocessed data) showing direct, step-free sputtering of the h-BN layer to vacuum, confirming the monolayer nature of the h-BN film.

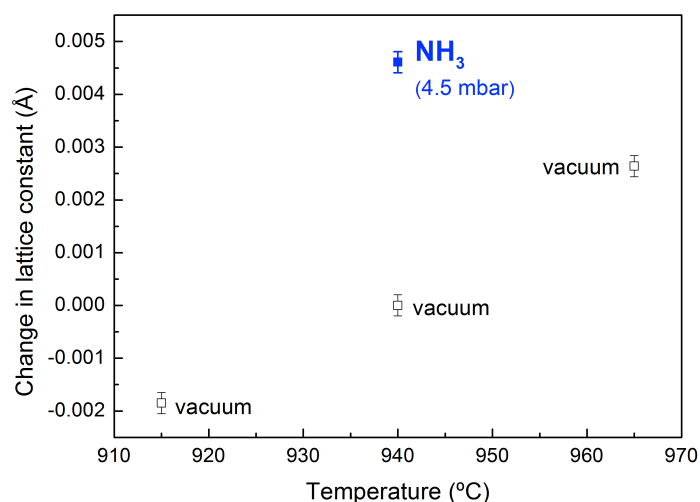


Figure S5. Change in γ -Fe lattice parameter of a Fe(500nm)/SiO₂(300nm)/Si sample during vacuum and NH₃ exposure (~4.5 mbar, 15 min) at 940 °C (corrected for thermal expansion via measuring a baseline temperature series in vacuum). Quantitative lattice parameters were derived by Rietveld refinement of bulk sensitive XRD measurements (using X'Pert Plus and file 44862 from the Inorganic Crystal Structure Database (ICSD)). A lattice shift corresponding to ~0.0045 Å was measured and is indicative of interstitial uptake of N into the γ -Fe lattice. Conversion from lattice shift to atom-% is according to phase diagram reference data¹ and suggests that ~0.6 atom-% N are interstitially dissolved in the γ -Fe lattice.

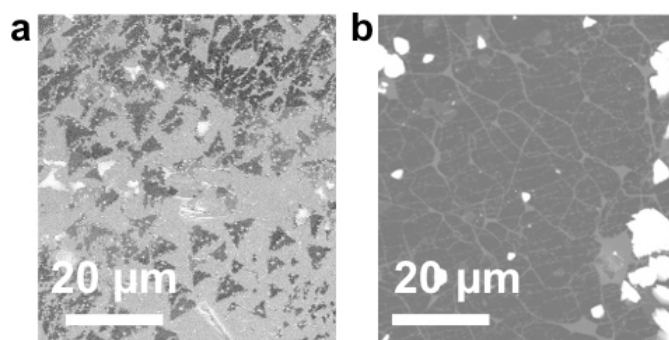


Figure S6. SEM images of (a) H₂-preannealed and (b) NH₃-preannealed Fe foils, corresponding to the samples in Figure 6. The in situ XPS experiments were performed at ~ 0.5 mbar annealing gas pressure, followed by h-BN growth (~ 900 °C, $\sim 1 \times 10^{-4}$ mbar, ~ 10 min).

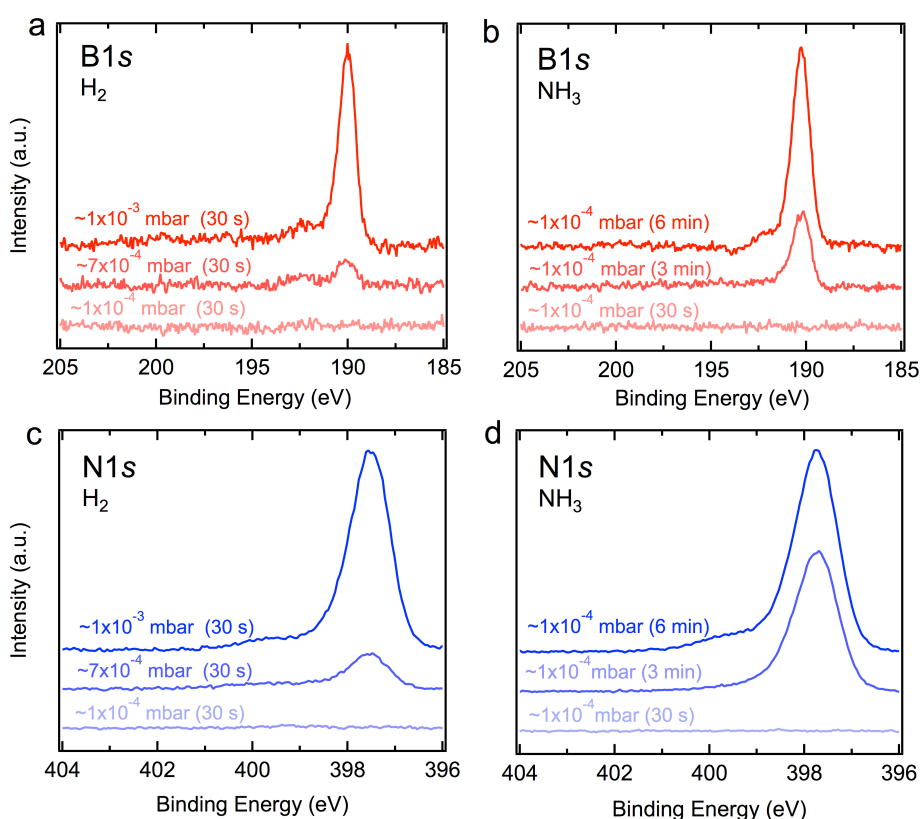


Figure S7. XP spectra of the initial stages of borazine dosing at ~ 900 °C, showing the B1s core level for (a) H₂-preannealed foil (immediately after setting the pressure at $\sim 1 \times 10^{-4}$ mbar, $\sim 7 \times 10^{-4}$ mbar and $\sim 1 \times 10^{-3}$ mbar) and (b) NH₃-preannealed foil (acquired immediately after reaching $\sim 1 \times 10^{-4}$ mbar, and after 3 min and 6 min at the same pressure, and the N1s core level for (c) H₂-preannealed Fe foil and (d) NH₃-preannealed foil (acquired at the same times and pressures as the corresponding B1s spectra).

References

- (1) Wriedt, H. A.; Gokcen, N. A.; Nafziger, R. H. *Bull. Alloy Phase Diagrams* **1987**, 8, 355–377.