

Supplementary material:

Molecular beam epitaxial growth of hexagonal boron nitride on Ni foils

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1. Grain size and orientation distribution in the polycrystalline Ni foils

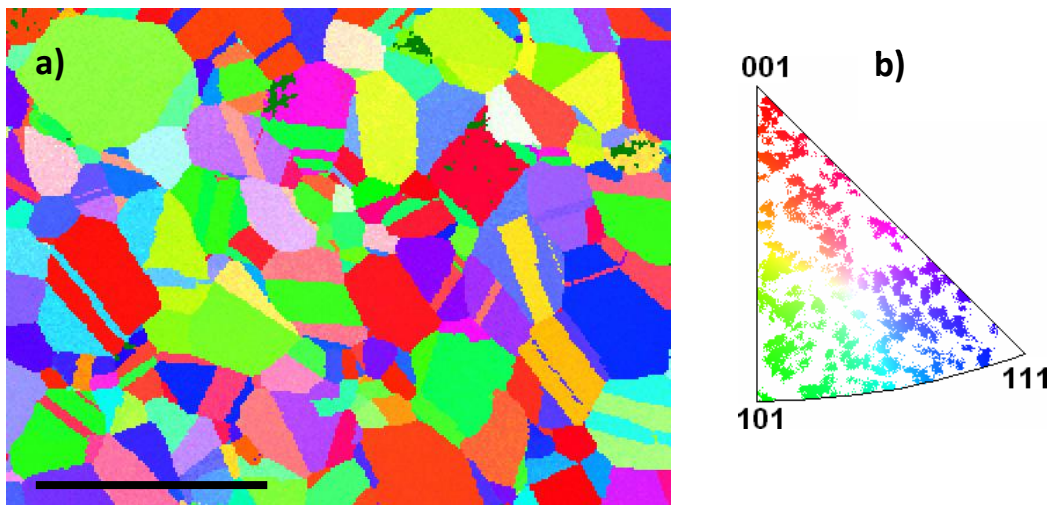


Figure S1: A reference Ni foil after a 1000°C anneal under ultra-high-vacuum, electron backscattered map showing the distribution of the grain orientations (a) and the corresponding inverse pole figure (b). The scale bar in (a) is 200 μm .

2. BN transfer process

This process was initially developed to transfer graphene [1] and is detailed in this article. In short, it involves 6 steps as follows:

- 1) PMMA deposition on the BN layer to be transferred

- 2) backside BN etched under O₂ plasma exposure
- 3) Ni foil wet etching in a solution of 20 g of FeCl₃ diluted in 100 ml deionized water, at 60°C
- 4) transfer on a Si substrate and drying
- 5) UV exposure
- 6) solvent-assisted PMMA removal

All steps except the 3rd one are identical to the graphene on Cu transfer process described in [1].

3. Large energy range B1s XPS spectrum

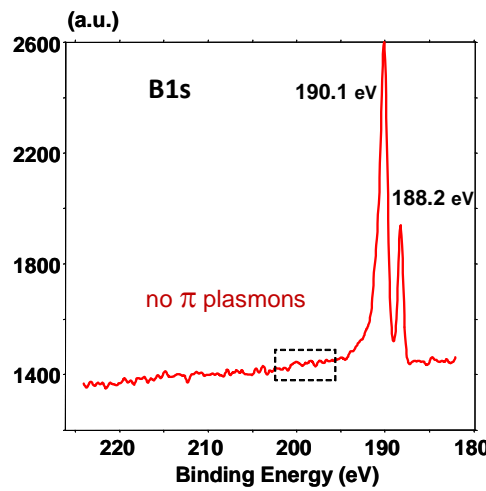


Figure S2: XPS core level spectra for B1s after growth for 2 hours at 800°C with $P_{\text{borazine}} = 3.5 \times 10^{-8}$ Torr. The π plasmon peak is not detected in the marked energy range.

4. BN thickness estimation from XPS measurements

In order to estimate the thickness of BN, we used the Beer Lambert equation [2] associating the intensity I of the emitted photoelectrons to the material depth z and to the electron inelastic mean free path λ . This equation reflects the photoelectron extraction mechanism, which is the depth-limiting effect in XPS analysis.

$$dI(z) = N \cdot \sigma \cdot T \cdot \phi \cdot A \cdot e^{\frac{-z}{\lambda \sin \theta}} dz \quad (\text{S1})$$

N Atomic density of the probed material

σ Effective photoionization cross section of the probed material

T Transmission factor of the spectrometer depending on the electron kinetic energy

ϕ X-ray photon flux

A Section of the analyzed area

z depth from the surface at which the emission occurs

θ detection angle with respect to the surface plane

Based on equation S1 and on the experimental intensities of the peaks B1s, N1s & Ni2p3/2, we estimated the thickness of the deposited BN. For this, we assumed a homogeneous material of constant thickness (figure S2). We detail in the following the estimation of the thickness from the experimental intensity ratio I_B/I_{Ni} , the calculation being the same if we use the intensity ratio between the N and Ni peaks.

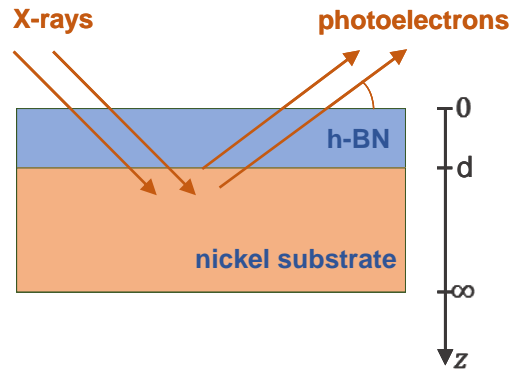


Figure S3: Constant thickness model scheme used to evaluate the BN thickness.

Assuming a bulk substrate composed of chemical element i , integrating the expression S1 from surface ($z=0$) to infinity gives the intensity I_i^0 :

$$I_i^0 = \int_0^\infty N_i \cdot \sigma_i \cdot T(E_i) \cdot \Phi \cdot A \cdot e^{\frac{-z}{\lambda \sin \theta}} dz = N \cdot \sigma \cdot T \cdot \Phi \cdot A_{90^\circ} \cdot \lambda \quad (S2)$$

where $A_{90^\circ} = A \cdot \sin \theta$.

Considering the Ni and B intensities, we obtain respectively :

$$I_{Ni}^0 = N_{Ni} \cdot \sigma_{Ni} \cdot T(E_{Ni}) \cdot \Phi \cdot A_{90^\circ} \cdot \lambda_{Ni,Ni} \quad (S3)$$

$$I_B^0 = N_B \cdot \sigma_B \cdot T(E_B) \cdot \Phi \cdot A_{90^\circ} \cdot \lambda_{B,BN} \quad (S4)$$

The different parameters correspond to :

N_B Atomic density of B in h-BN (0.055 atoms/Å³)

N_{Ni} Atomic density of Ni (0.092 atoms/Å³)

σ_B B photoionisation cross section for the Al K α line

σ_{Ni} Ni photoionization cross-section

$T(E_{Ni})$ Transmission factor of the spectrometer at the Ni photoelectron kinetic energy

$T(E_B)$ Transmission factor of the spectrometer at the B photoelectron kinetic energy

A_{90° Section of the analyzed area at 90°.

$\lambda_{Ni,Ni}$ Inelastic mean free path of photoelectrons released from Ni through Ni

$\lambda_{B,BN}$ Inelastic mean free path of photoelectrons released from boron through BN

To simplify photoemission measurements, atomic sensitivity factors S_i are usually provided by spectrometer manufacturers for each chemical element as well as for electronic transitions. These factors make it possible to relate the atomic density N_i to the intensity I_i^0 .

$$I_{Ni}^0 = N_{Ni} \cdot S_{Ni} \quad (S5)$$

$$I_B^0 = N_B \cdot S_B \quad (S6)$$

The sensitivity factors for Ni, B and N were directly measured on reference samples for the X-ray source used in our experiments (Al K α radiation), from which relative sensitivity factors $S_B/S_{Ni} = 0.103$ and $S_N/S_{Ni} = 0.339$ were deduced. The intensity of the B1s signal emitted through a homogeneous BN layer of thickness d is obtained by integrating equation S1 from the surface ($z=0$) to the interface ($z=d$) :

$$I_B = \int_0^d N_B \cdot \sigma_B \cdot T \cdot \Phi \cdot A \cdot e^{\frac{-z}{\lambda_{B,BN} \sin \theta}} dz = N_B \cdot \sigma_B \cdot T \cdot \Phi \cdot A_{90^\circ} \cdot \lambda_{B,BN} \cdot \left(1 - e^{\frac{-d}{\lambda_{B,BN} \sin \theta}} \right) \quad (S7a)$$

$$I_B = I_B^0 \cdot \left(1 - e^{\frac{-d}{\lambda_{B,BN} \sin \theta}} \right) \quad (S7b)$$

The intensity of the Ni2p3/2 component is already calculated in equation S3, but we have to take into account now the attenuation of the electrons coming from the Ni substrate through the BN layer :

$$I_{Ni} = I_{Ni}^0 \cdot \left(e^{\frac{-d}{\lambda_{Ni,BN} \sin \theta}} \right) \quad (S8)$$

where $\lambda_{Ni,BN}$ is the mean free path of photoelectrons released from Ni through BN. By calculating the ratio between equations S7b and S8, we obtain :

$$\frac{I_B}{I_{Ni}} = \frac{S_B \cdot N_{B,BN}}{S_{Ni} \cdot N_{Ni}} \frac{[1 - e^{\frac{-d}{\lambda_{B,BN} \sin \theta}}]}{e^{\frac{-d}{\lambda_{Ni,BN} \sin \theta}}} \quad (S9)$$

The terms S_B , $N_{B,BN}$, S_{Ni} and N_{Ni} are constants. They can be replaced by a constant $\alpha_{B/Ni}$:

$$\frac{S_B \cdot N_{B,BN}}{S_{Ni} \cdot N_{Ni}} = \alpha_{B/Ni} \quad (S10)$$

The I_B/I_{Ni} ratio is thus expressed as follows:

$$\frac{I_B}{I_{Ni}} = \alpha_{B/Ni} \frac{[1 - e^{\frac{-d}{\lambda_{B,BN} \sin \theta}}]}{e^{\frac{-d}{\lambda_{B,BN} \sin \theta}} \frac{\lambda_{B,BN}}{\lambda_{Ni,BN}}} \quad (S11)$$

We finally derive an equation of the form $f(x)=0$, where $x=d/\lambda_{B,BN}$:

$$f(x) = \frac{I_B}{I_{Ni}} - \alpha_{B/Ni} \frac{\left[1 - e^{\frac{-x}{\sin \theta}} \right]}{e^{\frac{-x}{\sin \theta}} \frac{\lambda_{B,BN}}{\lambda_{Ni,BN}}} = 0 \quad (S12)$$

The ratio $d/\lambda_{B,BN}$ is calculated by solving this equation [S12](#) using the experimentally determined I_B/I_{Ni} ratio, and an inelastic mean free path ratio $\lambda_{B,BN}/\lambda_{Ni,BN}=1.82$ [\[3\]](#), from which the BN thickness d can be estimated.

5. BN thick domain distribution

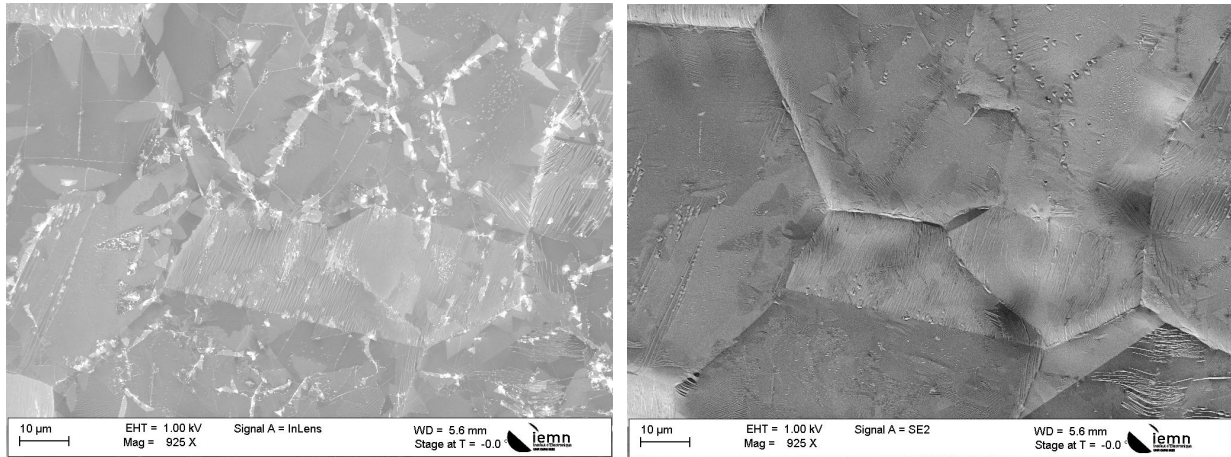


Figure S4: SEM images in InLens (left) and Everhart-Thornley SE2 mode (right) of the same area of a sample grown at 800°C for 2 h with $P_{\text{borazine}} = 3.5 \times 10^{-8}$ Torr, showing the alignment of the thick BN domains. Thick BN triangular domains are best observed in InLens mode, while the SE2 mode is used to image the grain boundaries.

References:

- [1] G. Deokar, J. Avila I. Razado-Colambo, J.-L. Codron, C. Boyaval, E. Galopin, M.-C. Asensio, & D. Vignaud, *Towards high quality CVD graphene growth and transfer*, Carbon, 89, 82, (2015).
- [2] H. Adrian, *Large Scale Single Layer Hexagonal Boron Nitride Growth, Process Control and Application*, PhD thesis, University of Zurich (2014).
- [3] C. J. Powell et al., *NIST Electron Effective-Absorption-Length Database*, Version 1.3, Standard Reference Data Program Database 82, National Institute of Standards and Technology, Gaithersburg, MD, (2011). <https://www.nist.gov/srd/nist-standard-reference-database-82>.