

## Supporting Information

### Towards the Controlled Synthesis of Hexagonal Boron Nitride Films

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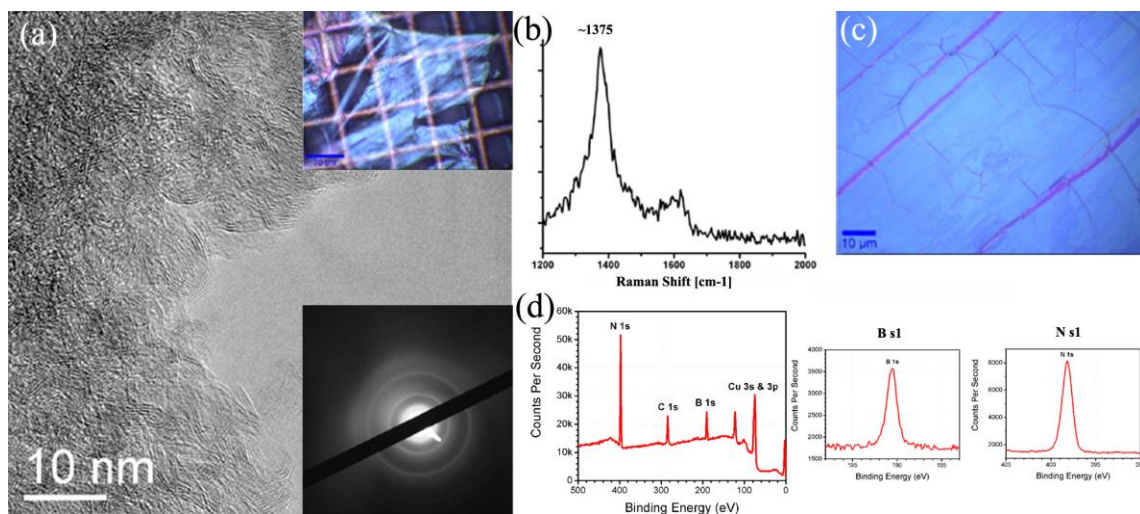
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## The Growth and Characterization of BN on Cu foils

The growth of BN films on Cu foils (99.98%, Alfa Aesar) was carried out with similar conditions to those for Ni foils (as described in the manuscript). The CVD process conditions used are: temperature range 650-1025 °C, diborane:ammonia ratio of 1:18 and 1:9, and growth times from 1 to 30 mins. All of the films obtained from these experiments had only an n-BN (t-BN) phase as shown in Figure SI 1.



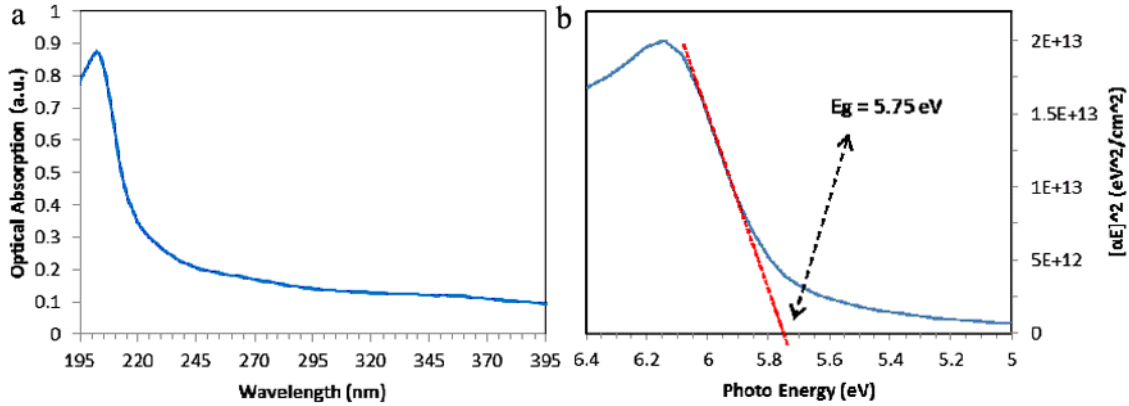
**Figure SI 1:** Characterization of n-BN (t-BN) grown on Cu foil: (a) TEM image showing the nanocrystalline structure, the top and bottom right insets show an optical image of the film on the TEM grid and the SAED. (b) Raman spectrum of the film shown in the optical micrograph in (c). (d) XPS characterization of the same film showing a B:N ratio of 49:50 at. %.

## UV-Visible Spectroscopy

UV-Visible spectra were obtained to measure the optical properties of the films (Cary 5000 UV-VIS NIR Spectrometer). The measurement was taken in dual beam mode with the blank quartz slide in the reference position. Data were acquired over a wavelength range of 900-200 nm. For a direct band-gap semiconductor, the optical band-gap energy can be determined by the equation:<sup>1, 2</sup>

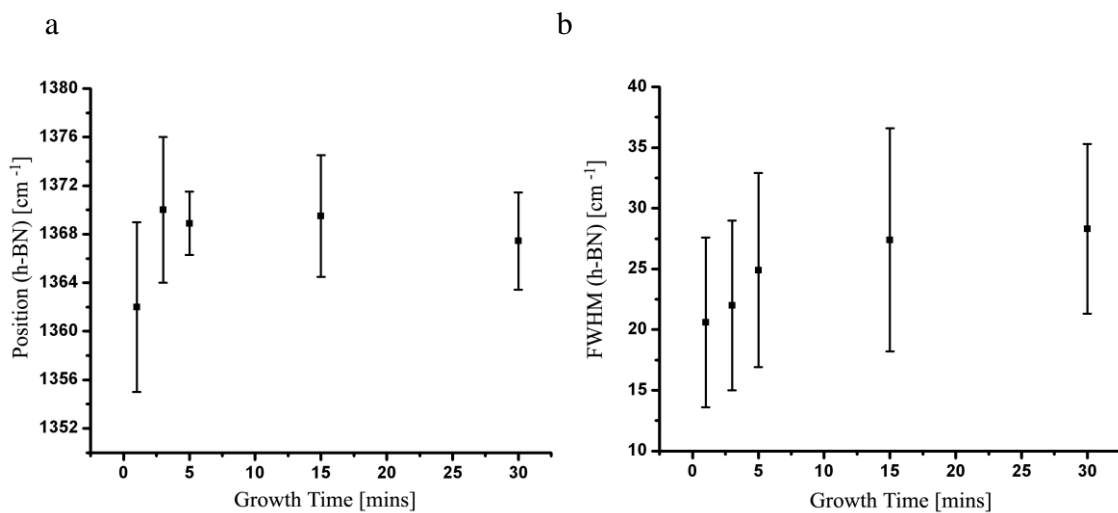
$$(1) \quad \alpha = A \left( \frac{E - E_g}{E} \right)^{1/2}$$

Where  $\alpha$  is the absorption coefficient,  $A$  is a constant,  $E$  is the photon energy and  $E_g$  is the band-gap energy. By plotting  $(\alpha E)^2$  as a function of  $E$ , the band-gap energy can be estimated by extrapolation to the x-axis.<sup>1, 2</sup> We extracted a band-gap of 5.75 eV which is slightly lower than the value measured for thin films reported by others, 5.9-6 eV,<sup>3, 4</sup> and bulk h-BN, ~5.85 eV.<sup>5, 6</sup> This discrepancy may arise from the stacking order between the layers and/or strain in the film<sup>7, 8</sup>.



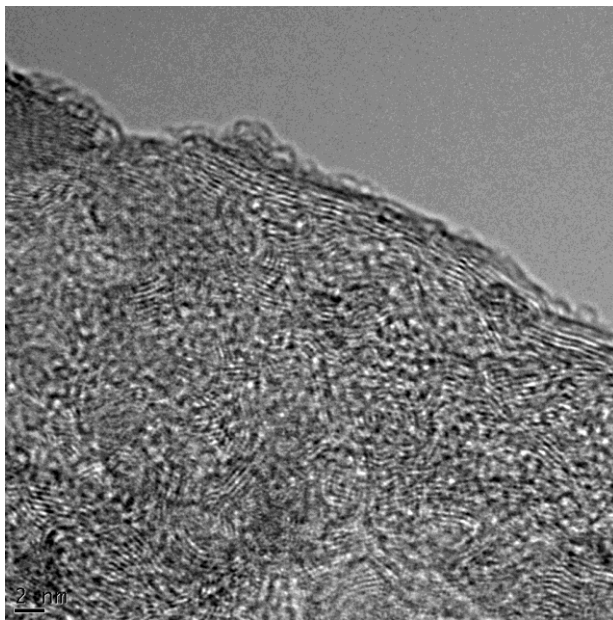
**Figure SI 2:** UV-VIS characterization. (a) Optical absorption as a function of incident wavelength. (b) Calculation of the optical band-gap by plotting  $(\alpha E)^2$  as a function of  $E$ . The extrapolation of the straight region (red line) and its intersection with the  $E$  axis, gives an estimation of the band-gap energy.

## Raman Mapping Analysis

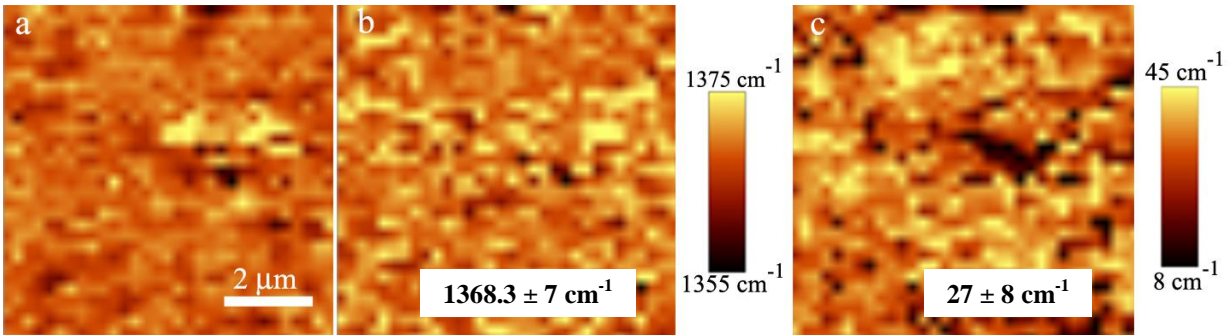


**Figure SI 3:** Analysis of the position, (a), and FWHM, (b), of the h-BN peak as a function of growth time.

## CVD Growth at 800° C on Ni foil



**Figure SI 4:** TEM image of h-BN film grown at 800°C for 15 mins showing a nanocrystalline structure, n-BN (turbostratic, t-BN).



**Figure SI 5:** 2D Raman mapping of h-BN on sapphire. Mapping with the intensity, (a), position, (b) and FWHM, (c) of the h-BN peak. The insets in (b) and (c) are the average and the standard deviation calculated from the mapping on tens of micron square areas, respectively.

**XPS Data: Table SI 1**

	B-N (B 1s)		B-N (N1s)		B:N	B-O (B 1s)		Ni-B (B 1s)		Ni (Ni 2p)	
	Position (eV)	at %	Position (eV)	at %		Position (eV)	at %	Position (eV)	at %	Position (eV)	at %
Thick h-BN (CVD)	191.13	34.25	398.76	33.24	1.03	none	none	none	none	852.89	0.52
Thick h-BN (CVD) after sputter	191.09	41.61	398.59	37.04	1.12	none	none	188.98	6.61	852.88	0.77
SG*- B <sub>2</sub> H <sub>6</sub> first	190.6	22.83	398.27	21.58	1.06	193.33	11.32	188.43	3.98	852.84	6.05
SG*- NH <sub>3</sub> first	190.66	29.62	398.34	35.87	0.82	none	none	none	none	852.84	4.14
B <sub>2</sub> H <sub>6</sub> ** exposure	none	none	none	none	NA	193.44	21.31	188.3	2.94	852.91	2.74
NH <sub>3</sub> ** exposure	none	none	none	none	NA	none	none	none	none	852.9	17.58

\* SG = Sequential-Growth

\*\* Control experiments: samples exposed to one precursor at the CVD temperature (1025 °C)

## References

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