Supporting Information

Characterization Methods

Fourier-Transformed Infrared Spectroscopy

The spectra were recorded using a Spectrum 400 (*Perkin Elmer)* in the range of 500-4000 cm^{-1} with four scans per sample, using a data interval of 1 nm and a scan speed of266.75 nm/min.

Scanning Microscope Spectroscopy

The SEM measurements were performed on a 300 VP RISE field emission scanning microscope (FESEM) from *Zeiss Sigma*.

Raman Spectroscopy

The Raman spectra were recorded using a Lab Ram HR 800 spectrometer (Horiba Ltd.) using a green line Ar$^+$ ion laser (514.5 nm) in the range of 900-2000 cm^{-1}.

X-Ray Photoelectron Spectroscopy

The XPS spectra were measured with an ESCA M-Probe spectrometer (*Surface Science Instruments)*. A monochromatic Al K$_\alpha$ x-ray source (1486.6 eV, λ = 8.33 Å) was used and the spectra were recorded in the range of 0-1000 eV at ultra-high vacuum (10^{-9} mbar). The survey spectra were recorded using the following parameters: detector pass energy: 158.3 eV; step size: 0.5 eV; dwell time: 125 ms; data accumulation: seven scans per sample. High resolution spectra were recorded using the following parameters: detector pass energy: 55.2 eV; step size: 0.05 eV; dwell time: 175 ms; data accumulation: ten scans per sample (carbon) and 25 (other elements) were chosen, respectively. The data was evaluated using CASA XPS software suite (*Casa Software Ltd.)*.

UV-Vis Measurement

The UV-vis spectra were recorded using a LAMBDA 950 spectrometer (*Perkin Elmer)*. The samples were measured in the transmission mode compared to a reference consisting of the same substrate material.

Atomic Force Microscopy

The measurement of the sample thickness and surface structure of the BN layers were carried out on a *XE-100* (*Park System*) atomic force microscope in a non-contact mode.

Transmission Electron Microscopy

High resolution transmission electron microscopy (HR-TEM) was carried out using a JEOL JEM 2200 FS equipped with UHR pole piece at 200 kV and an JEOL EDX detector. The thin

films were transferred onto Quantifoil® Multi A10 copper grids (200 mesh). Data analysis was carried out using ImageJ software suite and dedicated macros.

Contact Angle Measurement

The contact angles were measured with the drop shape analysis system DSA 100 (*KRÜSS GmbH)*. A defined amount (1 µL) of pure solvent (water, diiodomethane or ethylene glycol) is placed on the surface and the angle of the tangent between the baseline (substrate surface) and the solvent droplet is measured; each measurement is repeated on 3 independent positions and the resulting mean value is reported.
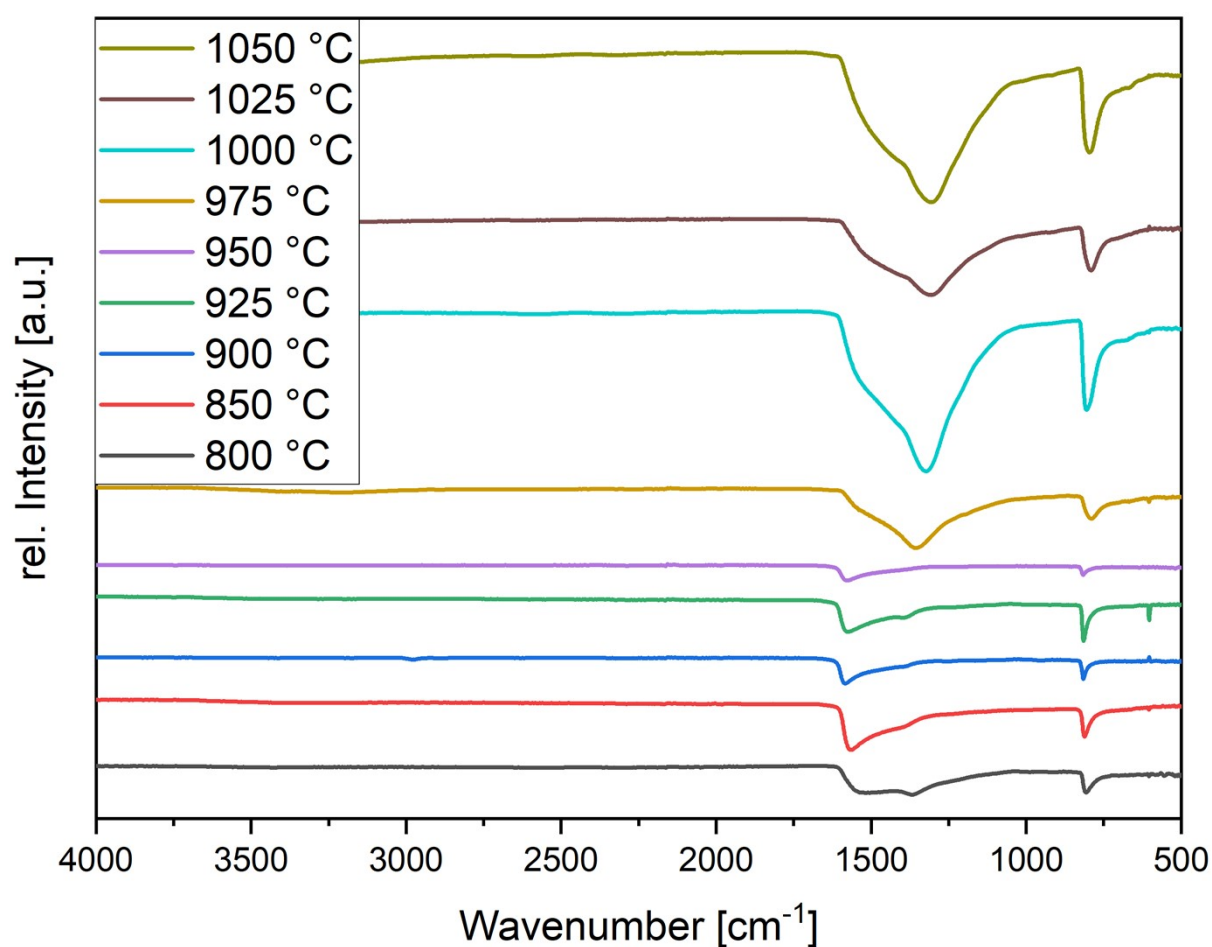

SI-Figure 1: ATR-FT-IR measurements of boron nitride depositions using ammonia borane depending on the temperature in the range of 800-1050 °C.

SI-Table 1: Position and intensity of the FT-IR vibrations of SI-Figure 1 depending on the temperature.

| Deposition Temperature [°C]	B-N-B out-of plane Vibration [cm⁻¹]	B-N in-plane Vibration [cm⁻¹]	N-H bond Vibration [cm⁻¹]
800	805 [87%]	1370 [86%]	1515 [86]
850	811 [80%]	-	1566 [74%]
900	817 [89%]	-	1584 [87%]
925	817 [78%]	1394 [88%]	1573 [82%]
950	815 [94%}	-	1578 [91%}
975	788 [83%]	1357 [70%]	-
1000	804 [55%]	1325 [27%]	-
1025	789 [77%}	1307 [66%]	-
1050	795 [54%]	1307 [32%]	-
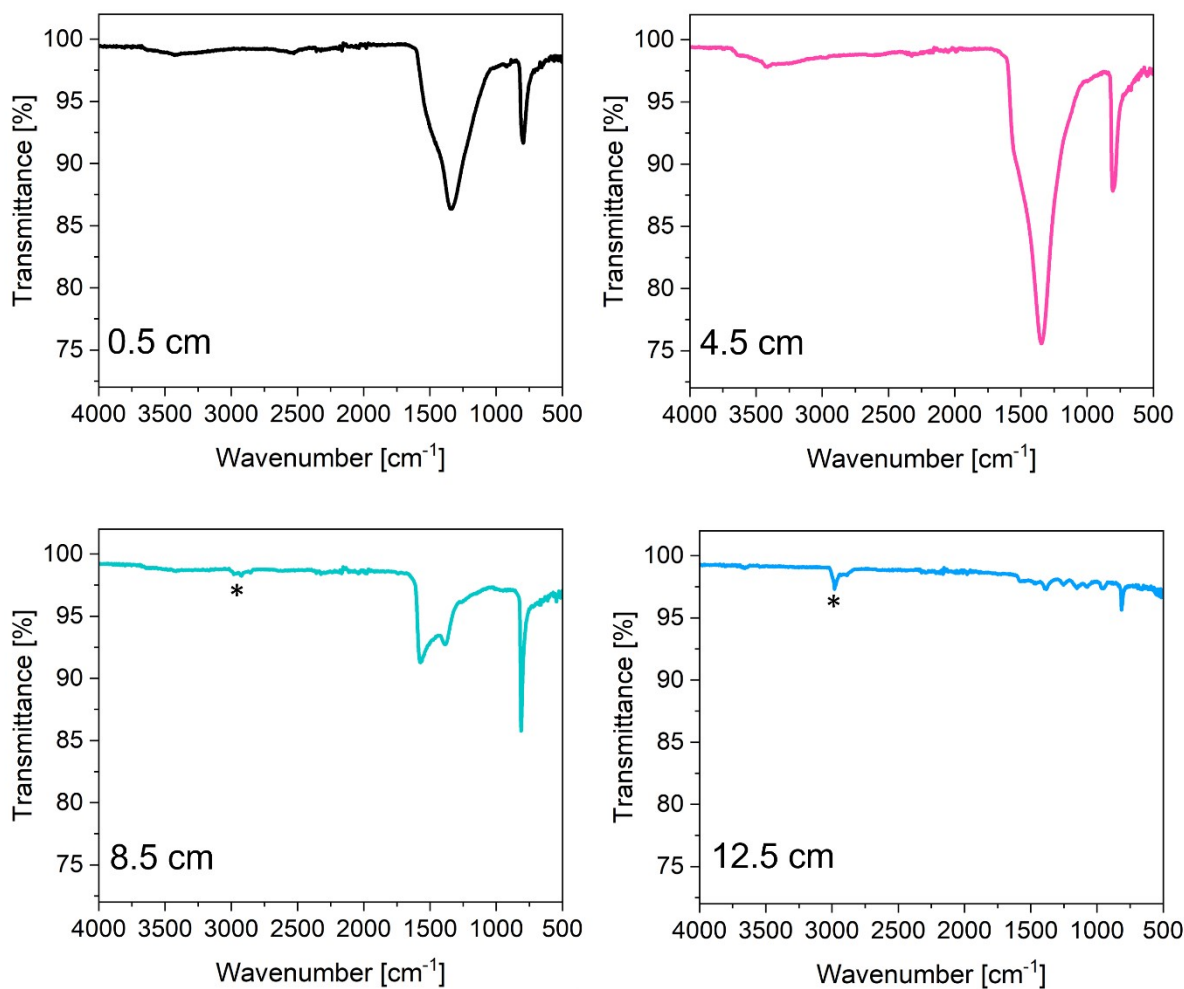
SI-Figure 2: Magnification of the FT-IR spectra of Figure 3. Deposited *h*BN thin films in hot-wall CVD using ammonia borane as precursor.
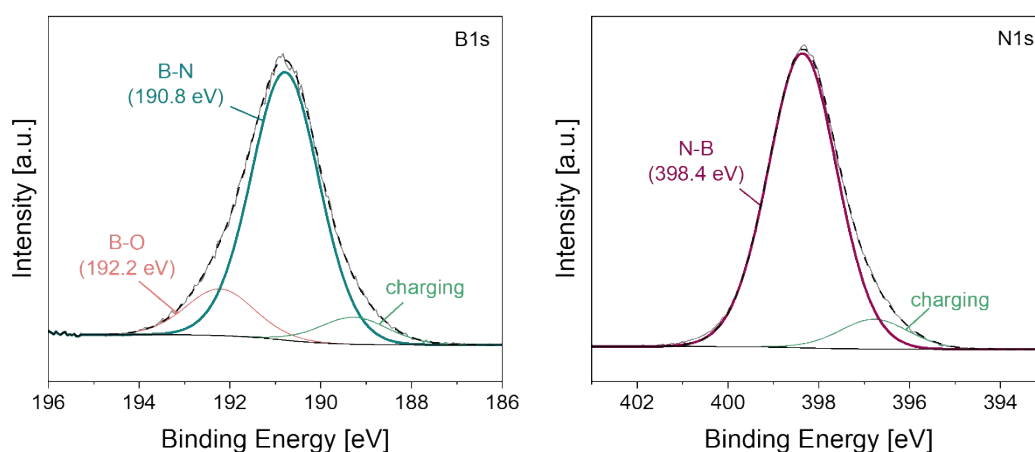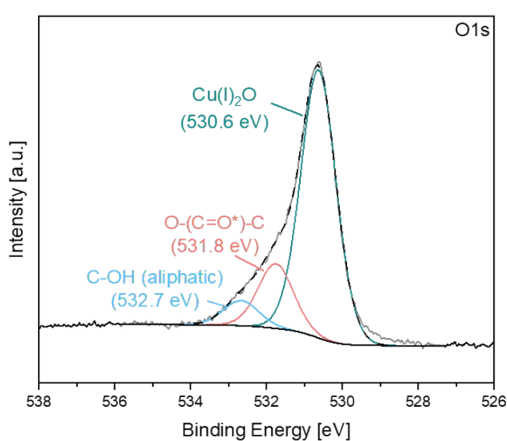

SI-Figure 3: Magnification of the high resolution XPS spectra of Figure 4. Deposited *h*BN films in a hot-wall CVD using ammonia as precursor.
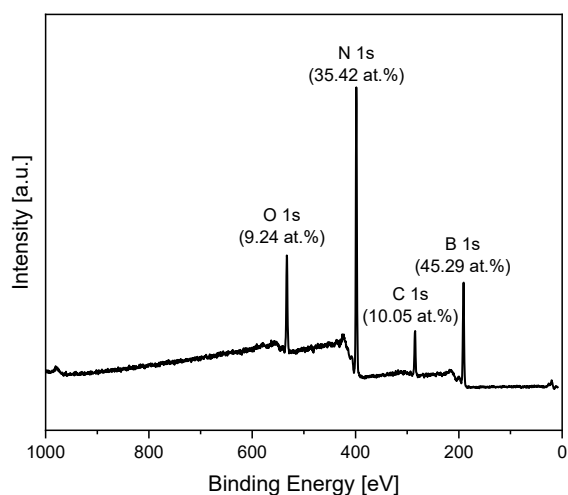
SI-Figure 4: Survey XPS spectra of *h*BN thin films deposited via hot-wall CVD using ammonia borane as precursor.
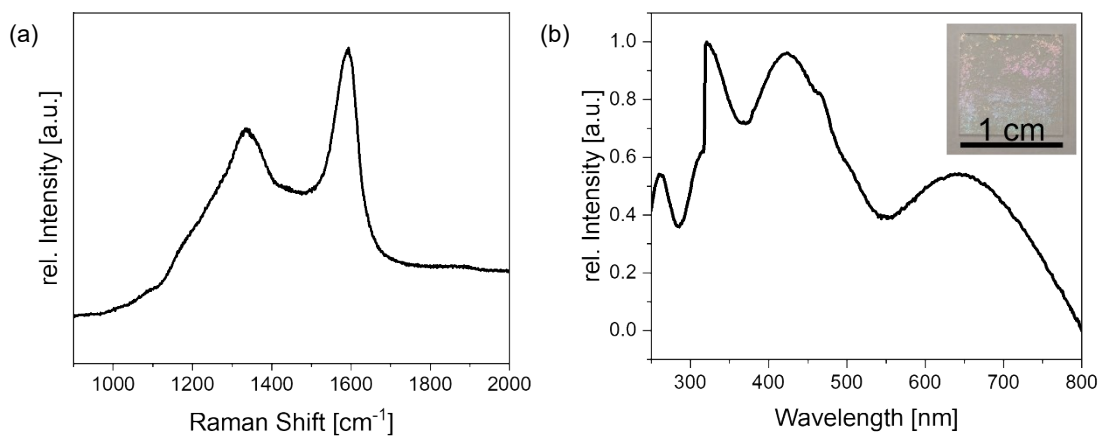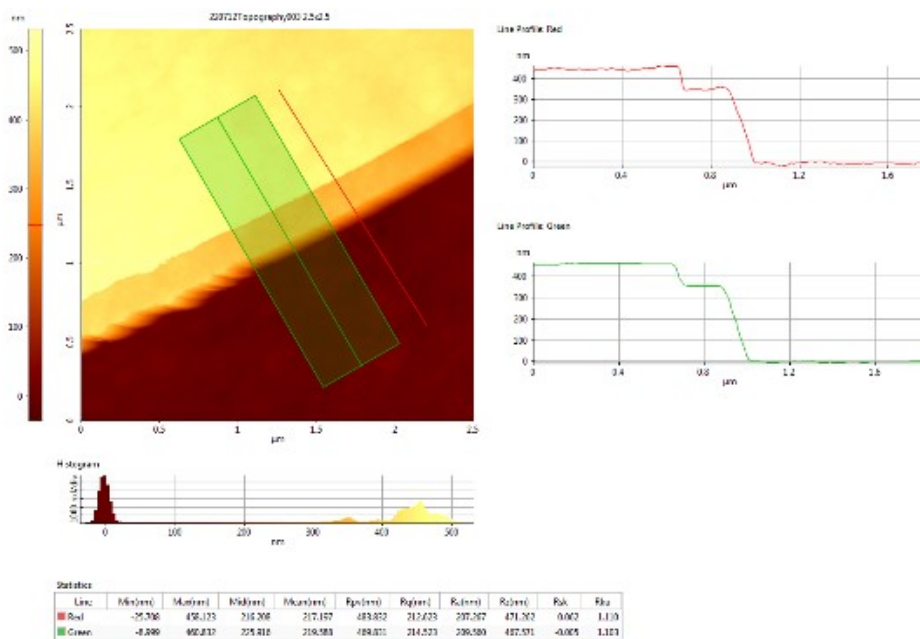

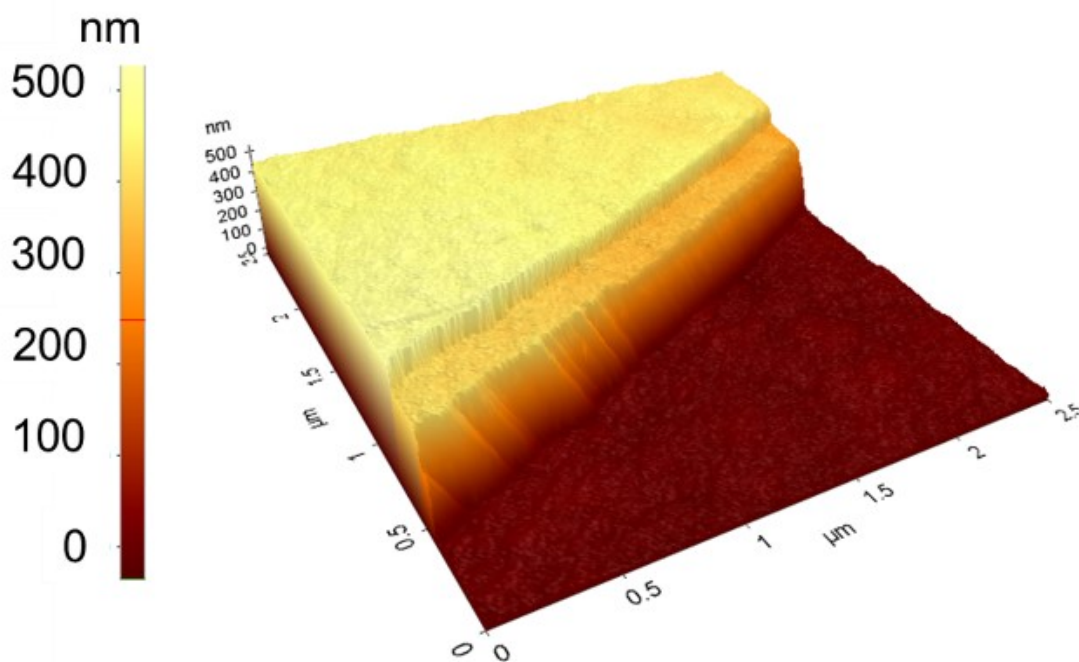*SI-Figure 5:* Magnification of the (a) Raman and (b) UV-vis spectra of Figure 4.

SI-Figure 6: High resolution spectra of the O1s core level XPS spectra of *h*BN thin films deposited via hot-wall CVD using borazine as precursor.
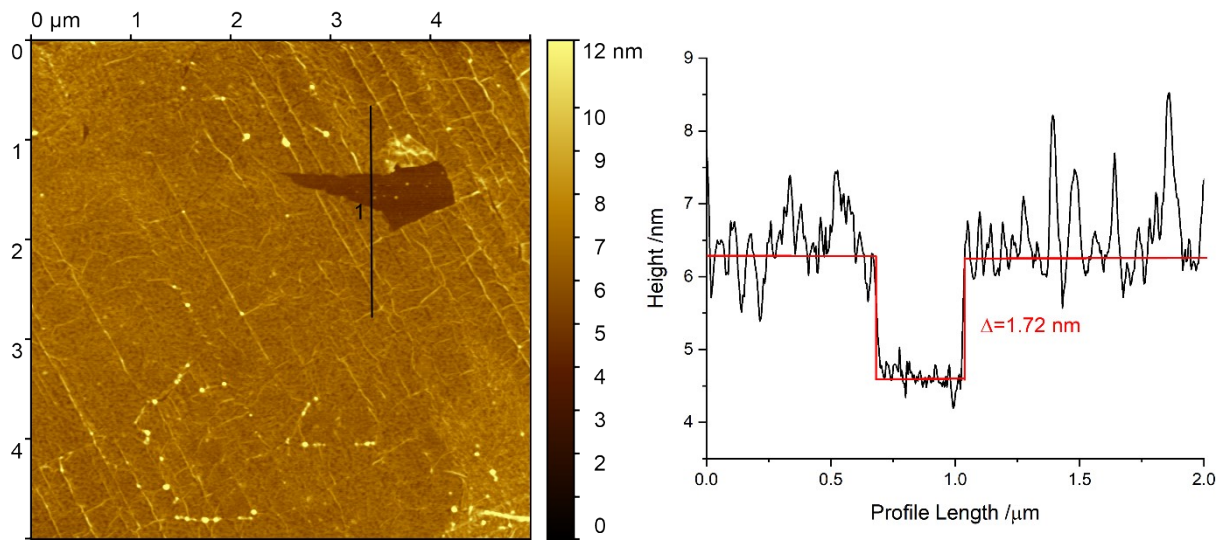
(a)

(b)

SI-Figure 7: (a) Details of the AFM measurement of *h*BN films deposited in a cold-wall CVD system with magnifications of the insets of (b) Figure 7.
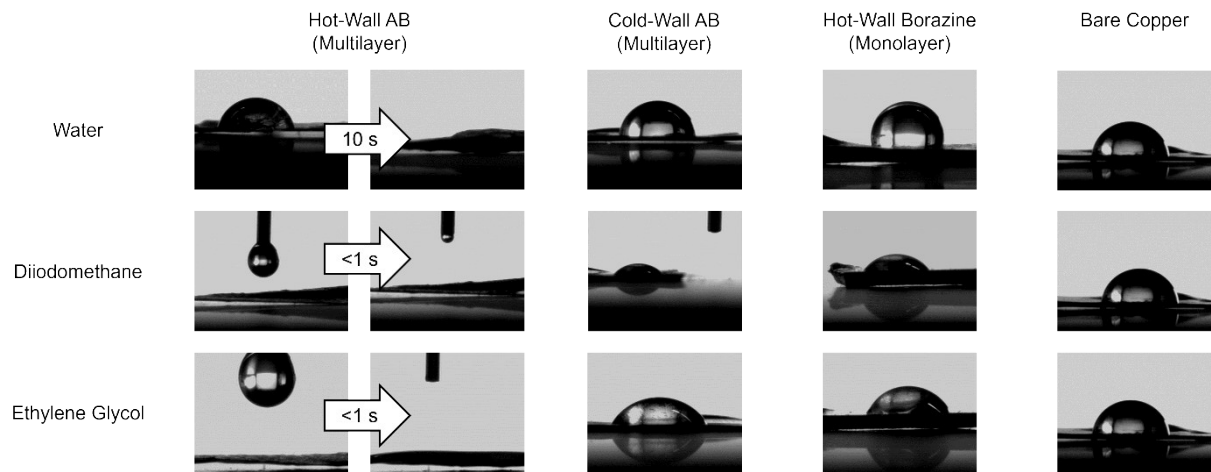
SI-Figure 8: Magnification of the AFM image of Figure 7. *h*BN thin film deposited by hot-wall CVD using borazine as precursor and transferred on SiO_2.

Determination of Surface Free Energy (SFE) according to the Fowkes relationship

The surface free energy (SFE) of a material can be determined by measuring the contact angles between the surface and solvents with known dispersive and non-dispersive components of their surface tension (SI-Table 2, SI-Figure 9).

SI-Table 2: Total surface tension as a sum of a dispersive and polar component for selected solvents used in this study. [1]

Liquid	Total surface tension / mN m-1	Dispersive component /mN m-1	Polar component /mN m-1
Diiodomethane (CH$_2$I$_2$)	50,8	50,8	0,0
Water (H$_2$O)	72,8	26,3	46,6
Ethylene glycol (EG)	48,0	29,8	18,2

SI-Figure 9: Contact angle measurements of *h*BN thin films deposited by hot and cold wall CVD using ammonia borane and borazine as precursor compared to a bare copper substrate. Water, diiodomethane and ethylene glycol were used as solvents for the measurement.

Based on the fundamental relationships formulated by Fowkes [2], the contact angle (θ) of a solvent with a surface tension only consisting of a disperse components σ_l^D (CH$_2$I$_2$), the disperse component of the surface energy σ_s^D can be obtained (eq.1). In a subsequent step, the polar component σ_s^P can be derived from the contact angle (θ) of a second solvent (H$_2$O) with known polar (σ_l^P) and disperse (σ_l^D) components of the surface tension (eq. 2).

$$cos\theta = 2\sqrt{\sigma_s^D} \cdot \frac{1}{\sqrt{\sigma_l^D}} - 1 \qquad \text{(eq. 1)}$$

$$2\sqrt{\sigma_l^P} \cdot \sqrt{\sigma_s^P} = \sigma_l(cos\theta + 1) - 2\sqrt{\sigma_s^D \cdot \sigma_l^D} \qquad \text{(eq. 2)}$$

SI-Table 3: Summary of contact angles with different solvents and resulting surface energies according to the Fowkes relationship. Wherever possible, the contact angle was measures at three independent positions at each sample and the mean value and corresponding standard deviation is reported. Due to the inability to determine the quasi-non-existent contact angles between the hBN coating derived from ammonia borane in a hot-wall setup with CH_2I_2 and EG the dispersive components can only be estimated, but due to the low contact angles observed (<5°) the error can be estimated to be less than 1% for the dispersive component.

Precursor (Process)	Contact Angle /°			Surface Energy /mJ m-2)		
	H_2O	CH_2I_2	EG	Dispersive component	Polar component	Total
Reference (Cu Substrate)	76.0 ± 2.0	75.3 ± 0.7	74.7 ± 3.6	20.0 ± 0.4	5.5 ± 0.8	**25.9 ± 1.3**
Ammonia borane (Cold-Wall)	85.1 ± 3.5	53.0 ± 1.3	64.8 ± 2.2	32.6 ± 0.8	2.3 ± 1.0	**35.6 ± 1.7**
Ammonia borane (Hot-Wall)	33.3 ± 0.9	<5°	<5°	50.0 ± 0.4	30.3 ± 0.5	**80.7 ± 0.9**
Borazine (Hot Wall)	111.1 ± 1.0	51.2 ± 2.1	57.8 ± 2.7	33.6 ± 1.2	0.8 ± 0.2	**35.5 ± 1.3**

[1]   A. Zdziennicka, J. Krawczyk, K. Szymczyk, B. Jańczuk, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2017**, *529*,864-875.

[2]   F. M. Fowkes, *Industrial & Engineering Chemistry* **1964**, *56*,40-52.