## **Supplementary Information**

Epitaxial chemical vapour deposition growth of monolayer hexagonal boron nitride on Cu(111)/sapphire substrate

Yuki Uchida,<sup>a</sup> Tasuku Iwaizako,<sup>a</sup> Seigi Mizuno,<sup>a</sup> Masaharu Tsuji<sup>b</sup> and Hiroki Ago<sup>\*acd</sup>

<sup>a</sup>Interdiscriplinary Graduate School of Engineering Sciences, Kyushu University, Fukuoka 816-8580, Japan <sup>b</sup>Research and Education Center of Carbon Resources, Kyushu University, Fukuoka 816-8580 <sup>c</sup>Global Innovation Center (GIC), Kyushu University, Fukuoka 816-8580, Japan <sup>d</sup>PRESTO, Japan Science and Technology Agency (JST), Saitama 332-0012, Japan



**Fig. S1.** (a) AFM image of triangular h-BN grains transferred on a  $SiO_2$  substrate. (b) Height profile of a h-BN grain measured along the yellow line shown in (a).



**Fig. S2.** LEED patterns of as-grown h-BN films on Cu(111)/sapphire substrates, collected with different electron energies.



**Fig. S3.** XPS  $B_{1s}$  spectra of as-grown h-BN sheets. The peak is fitted with two Gaussian-Lorentzian mixed curves (Voigt function) which correspond to B atoms with sp<sup>2</sup> (~190.5 eV) and sp<sup>3</sup> (~191.1 eV) hybridized orbitals. We used the intensity of the sp<sup>2</sup> component to determine the [B]:[N] atomic ratio listed in Fig. 4, because only sp<sup>2</sup>-B atoms contribute to the h-BN formation. Excess sp<sup>3</sup>-B atoms may exist in the subsurface of Cu(111) and/or amorphous B at the interface between h-BN and Cu substrate.

	Peak position (eV)	Percentage of peak area (%)
sp <sup>2</sup>	190.3	69
sp <sup>3</sup>	190.9	31

Table S1. Fitting parameters used in Fig. S3.



**Fig. S4.** Optical micrograph of monolayer (a) and multilayer (b) h-BN films which were transferred on  $SiO_2/Si$  substrates ( $SiO_2$  thickness is 300 nm). Image (a) indicates that monolayer h-BN is difficult to be observed by an optical microscope. However, the edge was slightly recognized due to the presence of PMMA residue which was used to transfer the h-BN.



**Fig. S5.** (a) Optical microscope image of multilayer h-BN transferred on a  $SiO_2/Si$  substrate. (b) AFM image of the multilayer h-BN sheet. Here, monolayer or few-layer h-BN fully covers the Cu surface.



**Fig. S6.** SEM image of as-grown h-BN film on Cu(111) surface. Wrinkles are observed in the as-grown film .