

## Supporting Information

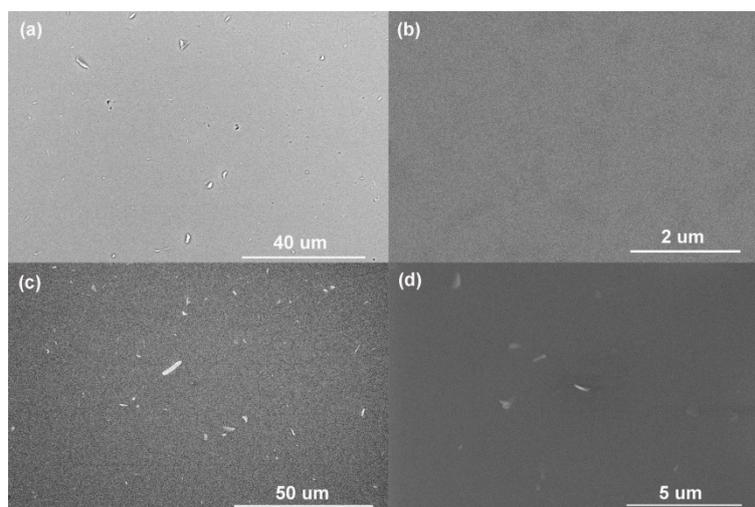
In the first group of experiments, the nucleation of c-BN films was studied according to the working gas. These c-BN films were prepared at a substrate bias voltage of  $-250$  V and a substrate temperature of  $470$  °C by using pure  $N_2$  and 1:1 Ar/ $N_2$ . The surface morphology of these films after deposition of 40 min was investigated by SEM. Figure S1 shows the typical SEM surface morphology of the films using pure  $N_2$  and 1:1 Ar/ $N_2$ . It can be seen that the film's surface is relatively smooth over a scale of hundreds of micrometers, though tiny features can be observed. Morphology information on the  $100$   $\mu\text{m}$  to several mm scale would validate use of these c-BN films in technological applications. We also observed the film surface by confocal microscopy, by which we actually observed almost nothing, as shown in Figure S2. Therefore, in order to observe the roughness or smoothness on an even larger area, Taly step using a  $0.1$   $\mu\text{m}$  stylus was utilized by monitoring different position of the surface. Herein, a  $200$  nm c-BN thin film was measured by Taly step. Figure S3a–c show typical profilographs of a tip moving on the film surface at different positions. There are also some noisy features on the surface; however, it seems homogeneous at least along the  $200$   $\mu\text{m}$  path. Moreover, we provide a SEM image (Figure S4) at the millimeter scale, which can provide information on the macroscopic scale.

On the other hand, concerning the surface morphology from a more microscopic view, typical AFM images with a scale of  $4$   $\mu\text{m} \times 4$   $\mu\text{m}$  recorded for each film are presented in Figure S5. From AFM measurements, these films are homogeneous at nanoscale.

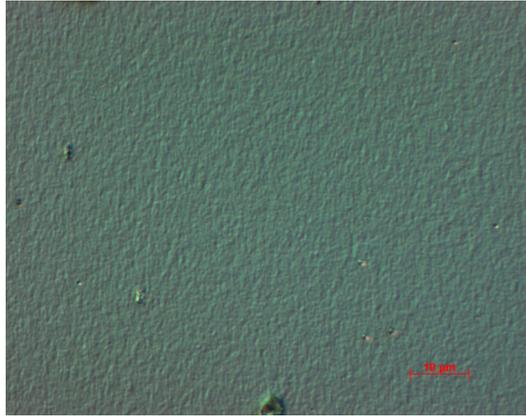
The template c-BN layers were prepared in pure  $N_2$  plasma under  $-250$  V substrate bias voltage at  $470$  °C for 30 min. Figure S6 shows a typical FITR spectrum, with a prominent TO c-BN peak at  $1079$   $\text{cm}^{-1}$  and two h-BN peaks. The cubic content is estimated to be 67%.

The surface chemistry was investigated by monochromatic XPS (Al  $K\alpha$ , radiation, photon energy  $1486.6$  eV). The binding-energy scale was calibrated in all cases by setting the Au  $4f_{7/2}$  binding-energy position to  $84.0$  eV. Figure S7a presents a typical XPS survey spectrum. It can be clearly seen that B  $1s$  at  $188$  eV and N  $1s$  at  $394$  eV correspond to c-BN films, and no other obvious peaks can be observed. Figures S3b and c show the core level spectra of B  $1s$  and N  $1s$ , respectively. The B:N composition ratio is estimated to be 0.98, close to 1:1.

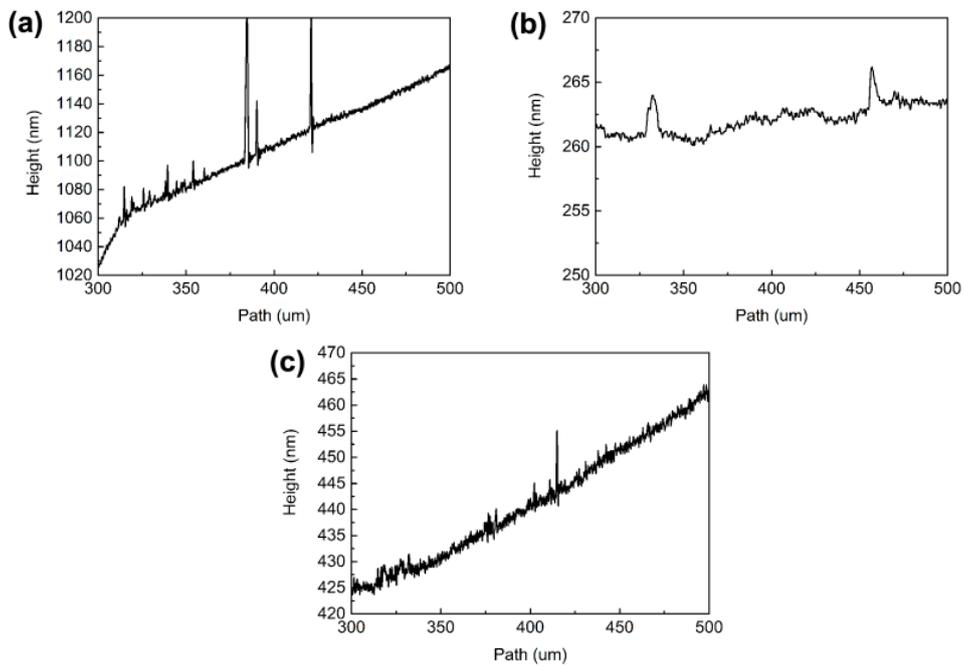
The surface morphology of this template c-BN film was studied by AFM and SEM. Figure S8a,b illustrate typical AFM and SEM images. It can be clearly seen that the film is composed of fine crystallites and is very smooth over a large area.



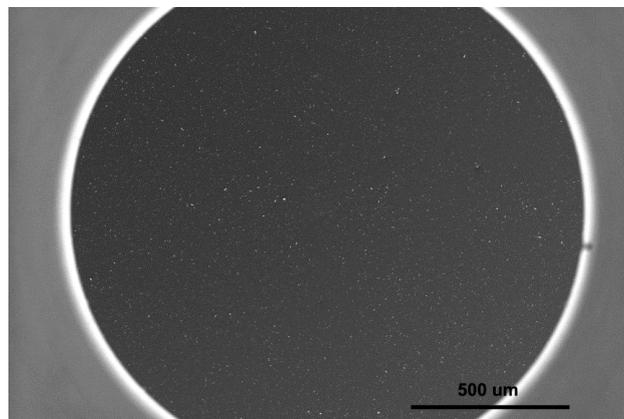
**Figure S1.** Typical SEM images of c-BN films grown using (a,b) Ar/ $N_2$  and (c,d) pure  $N_2$ .



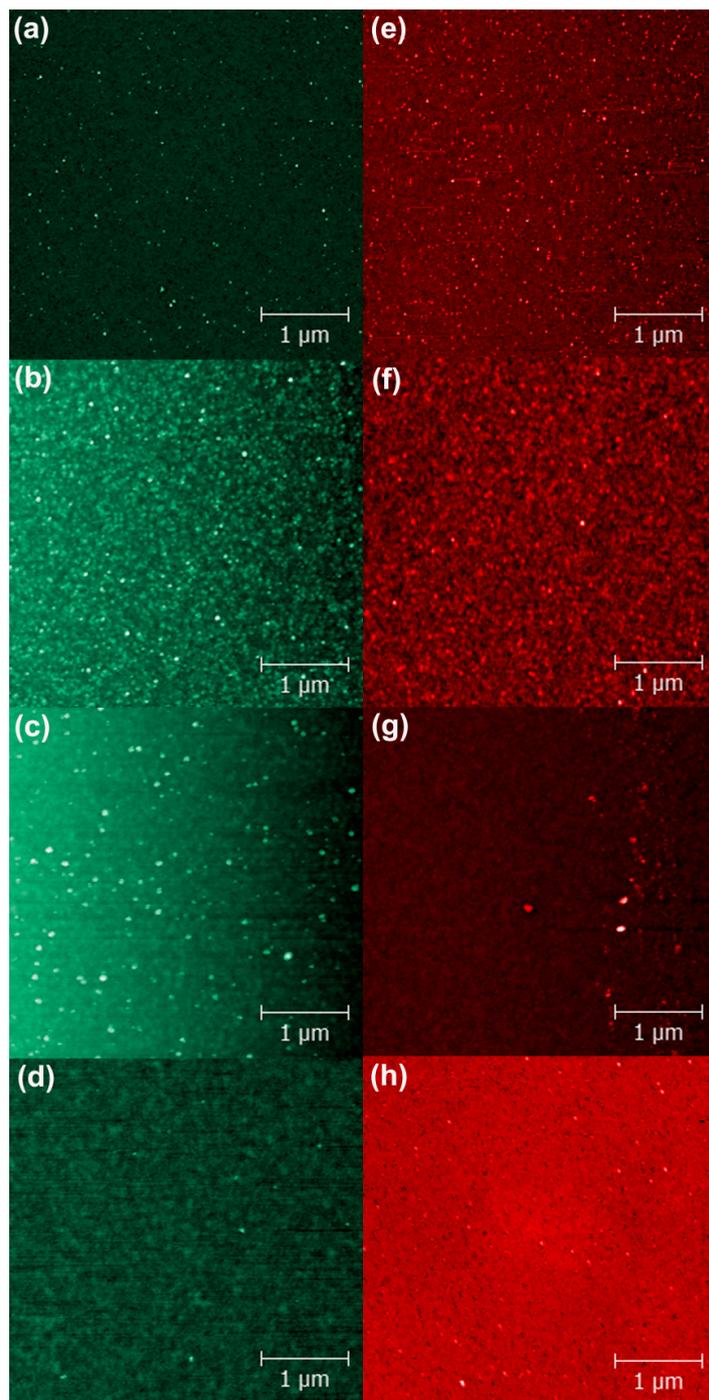
**Figure S2.** Typical confocal microscopy image of c-BN film grown using pure N<sub>2</sub>.



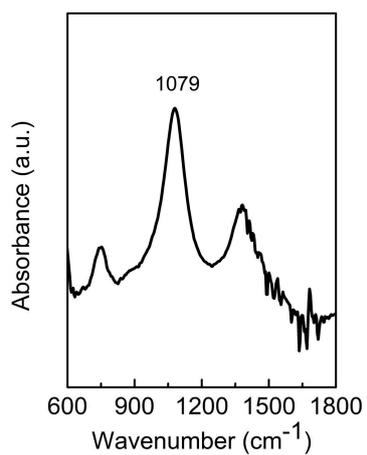
**Figure S3.** Typical Taly step profilographs of different positions (a–c) on a 200 nm thick c-BN film grown using pure N<sub>2</sub>.



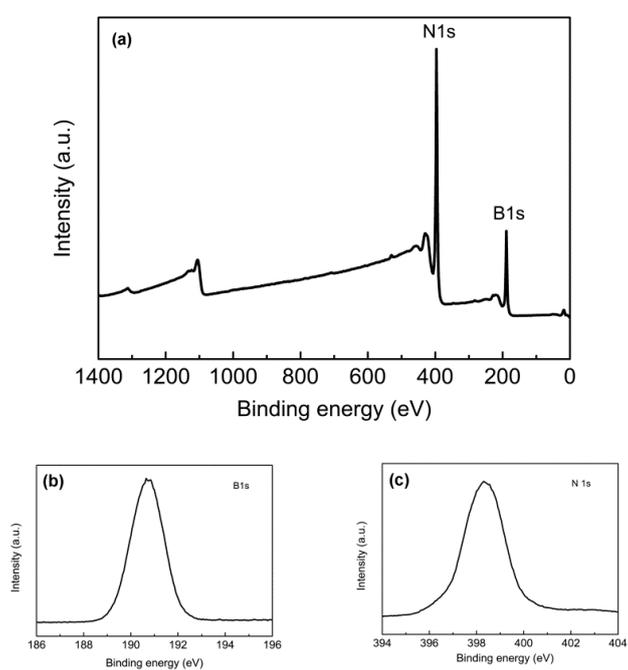
**Figure S4.** Typical SEM image of c-BN film grown using pure N<sub>2</sub>.



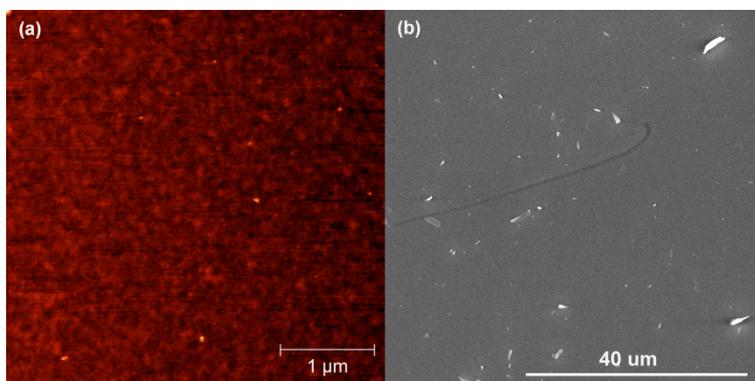
**Figure S5.** Typical AFM images of c-BN films grown using (a–d) pure N<sub>2</sub> plasma and (e–h) Ar/N<sub>2</sub> plasma: (a,e), (b,f), (c,g), and (d,h) for c-BN films with deposition times of 10, 20, 30, and 40 min, respectively.



**Figure S6.** FTIR spectrum of a typical c-BN template film used in the present work.



**Figure S7.** (a) XPS survey spectrum and core level spectra of (b) B 1s and (c) N 1s of a typical c-BN template film used in the present work.



**Figure S8.** (a) AFM and (b) SEM images of a typical c-BN template film used in the present work.