



Supplementary Materials: Self-Ordered Orientation of Crystalline Hexagonal Boron Nitride Nanodomains Embedded in Boron Carbonitride Films for Band Gap Engineering

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1. Heading

Figure S1: SEM images of the samples prepared in pure Ar with various substrate temperatures at (a) 250, (b) 400, (c) 500, and (d) 600 °C. The images of (e) and (f) are the samples prepared in pure Ar with a substrate temperature at (c) 500 and (d) 600 °C, respectively, collected with the sample tilting in an angle of 45° toward the SEM detector, Figure S2: SEM images of the samples prepared at substrate temperature of 500 °C with different N₂/Ar gas ratios of 0 (a), 0.2 (b), 0.4 (c), 0.6 (d), 0.8 (e), and 1 (f).

1.1. Subsection Heading

The BCN films with oriented crystalline h-BN nanodomains were prepared at various substrate temperatures in pure Ar gas on the Si substrate. The surface morphologies of these BCN films were inspected by SEM, indicating that the film surfaces become rougher with the increasing substrate temperature (Figure S1, Supplementary Materials). Column-like and even cone-like features emerge, especially for the film deposited at 600 °C. In order to observe the surface features more clearly, a cross sectional TEM image was taken for a film deposited with an r.f. power of 150 W and a bias voltage of -100 V at 600 °C, as illustrated in Figure 1a. The formation of a columnar structure with a conical surface can be clearly observed through the film growth direction. The thickness of this film is estimated as 175 nm. Figure 1b is a high-resolution TEM image taken from the selected area of the transition layer for this film. It exhibits one of the crystalline rod-like patches across the transition layer of a very high density. The width of these patches is about 5–18 nm, whilst the length is approximately 10-80 nm. The inset is the fast Fourier transformation (FFT) images of the selected area marked by the yellow square, which clearly shows the characteristic pattern of the normal orientation along the (0004) h-BN lattice planes, with an inter-planar distance of 0.186 nm at the entire regions of the patches. The lattice planes are slightly larger than that of the pure h-BN (0.167 nm), because of the C substitution. Figure 1c is a closer illustration of another selected area of the transition layer in this film. Figure 1d is the zoomed-in section of the selected area in Figure 1c, containing an inset of the h-BN atomic stacking model. From Figure 1d, the spacing of the adjacent white dots is 0.25 nm, corresponding to the nearest-distance between any of the same atoms of B or N within the chicken-wire layer [40]. It demonstrates a typical hexagonal symmetry, which indicates the singlecrystalline nature within this crystalline domain. Figure 1e illustrates an image taken from the very top of the film, in which a thin layer of amorphous material covers the outermost film continuously. This amorphous layer is about 3–4 nm thick, following the conical surface up and down. Thus, from the TEM observations, it intuitively indicates that the BCN films prepared in the present case mainly consist of rod-like h-BN nanodomains, with the basal planes perpendicular to the substrate and homogeneously distributed across the film. The Raman spectroscopy is expected to elucidate the chemical bonding state of the as-synthesized BCN films. Figure 1f shows the Raman spectra for a typical BCN film on Si substrate at 600 °C, as well as commercial graphite, synthesized h-BN, and a silicon substrate wafer. The measurements were performed at room temperature with a Renishaw spectrometer at 473 nm, with notch filters cutting at ~100 cm⁻¹. A tiny sharp peak at 1555 cm⁻¹ was clearly present in the Raman spectrum of the BCN film, coming from the Si substrate, indicating that our BCN film was of a high transparency. As compared to the h-BN sample with only one sharp E_{2g} peak at 1366 cm⁻¹, the Raman spectrum of the BCN film closely resembled that of graphite. Two broad bands were observed at 1382 and 1595 cm⁻¹, which are known as D and G band, respectively. The D band is usually assigned for distorted graphite, induced by the zone-boundary phonons activated by double resonance, and not just to the phonon confinement [41]. The G band corresponds to the E_{2g} phonon at the Brillouin zone center [42], which is reported to be moving from 1580 to 1600 cm⁻¹ [43]. Compared to the graphite sample, both the D and G bands of the BCN film blueshift and broaden to some certain extent. In the present case, the blueshift of the D band from 1366 to 1382 cm⁻¹ is understood as a consequence of the lattice defects, as it requires a defect for its activation. The origin of the weak G band upshifts of ~3 cm⁻¹ compared to the bulk graphite are partially due to the high hole doping induced phonon stiffening [43]. Our present BCN film contained a considerable amount of B, which will be discussed later. As the large downshift from 1600 to 1510 cm⁻¹ of the G band generally occurs for a completely disordered, almost fully sp²-bonded amorphous carbon consisting of distorted six-fold rings, the loss of the three-dimensional ordering can be excluded in the present case [44]. Unlike the spectrum of graphite, the exclusive presence of the broad features in the region of the low Raman frequency of the BCN film are commonly found in the spectra of boron-rich materials [45]. This will be evident from the energy dispersive X-ray spectroscopy (EDXS) and XPS measurements in the following. Thus, based on the aforementioned information, the formation of BCN films with highly crystalline oriented h-BN nanodomains is obtained by r.f. magnetron sputtering at higher substrate temperatures. Citing Figure S1.

The surface morphologies of the BCN films prepared at the varied substrate temperatures have been inspected by SEM, as illustrated in Figure S1. When the substrate temperature is lower than 250 °C, the surfaces of the B–C–N films are smooth, continuous, and have no pores in the large area scale. With the increasing substrate temperature, the film surfaces become rougher. The surface morphology of the BCN film prepared at room temperature is similar to the surface morphology of the BCN film prepared at 250 °C. Fine features emerge and gradually enlarge, especially for the film deposited at 500 and 600 °C. In order to observe the surface features more clearly, SEM images have been taken for these two films at an inclination of 45° (shown in Figure S1e,f). It can be unambiguously seen that the film surface exhibits as columnar and even conical when the substrate temperature varies from 500 to 600 °C. The height of the conical features increases at higher substrate temperatures.



Figure S1. SEM images of the samples prepared in pure Ar with various substrate temperatures at (a) 250, (b) 400, (c) 500, and (d) 600 °C. The images of (e) and (f) are the samples prepared in pure Ar with a substrate temperature at (c) 500 and (d) 600 °C, respectively, collected with the sample tilting at an angle of 45° toward the SEM detector.

In order to discern the effects of N_2 on the film morphology, BCN films prepared on the Si (100) substrate at a deposition temperature of 500 °C with a different N₂/Ar gas flow ratio were characterized by SEM. As shown in Figure S2 (Supplementary Materials), the surface morphologies of the BCN films are smooth and continuous in a large-scale area, regardless of the N₂/Ar gas ratio. Therefore, the microstructure of a film prepared with a N₂/Ar gas flow ratio of 1 was investigated by HRTEM. Figure 5 shows that turbostratic BN (t-BN) planes with a random orientation are formed within the BCN film matrix, as well as a tiny amount of BN nanocrystals (2-6 nm). As we know, t-BN is an analog to h-BN, but with randomly oriented basal planes. Unlike the vertically aligned h-BN nanodomains formed in the large background of amorphous BCN, the almost complete elimination of the amorphous fraction inside the film with the addition of N₂ lead to a higher kinetic condition, which may play an important role in the h-BN/c-BN phase equilibrium [60]. Under such a kinetic condition, the atomic mobility increased by high substrate temperatures is not sufficient enough to allow for the local bombardment-induced densifications to relax back to the thermodynamically stable h-BN phase. The h-BN/c-BN nucleation environment is gradually shifting. The formation of the curved and/or tilted t-BN basal planes observed here significantly prevents the growth of vertically oriented h-BN basal planes. In fact, these defective t-BN plane edges serve as c-BN nucleation sites as a result of the sp^3 character of the B–N–B bonds in the curled sp^2 bonded sheets [56]. Citing Figure S2.

As far as the surface morphology of the BCN films prepared at a substrate temperature of 500 °C with different N₂/Ar gas ratios shows, the SEM images in Figure S2 show no distinct tendency. The surface morphologies of the BCN films are smooth and continuous in a large area scale, regardless of the N₂/Ar gas ratio. Therefore, the film morphology is more sensitive to the substrate temperature.



Figure S2. SEM images of the samples prepared at a substrate temperature of 500 °C with different N₂/Ar gas ratios of 0 (**a**), 0.2 (**b**), 0.4 (**c**), 0.6 (**d**), 0.8 (**e**), and 1(**f**).



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