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Hexagonal boron nitride (h-BN) is an ideal substrate for two-dimensional (2D) materials because of its unique electrically insulating nature, atomic smoothness and low density of dangling bonds. Although mechanical exfoliation from bulk crystals produce the most pristine flakes, scalable fabrication of devices is still dependent on other more direct synthetic routes. To date, the most utilized method to synthesize large-area h-BN films is by chemical vapor deposition (CVD) using catalytic metal substrates. However, a major drawback for such synthetic films is the manifestation of thermally-induced wrinkles which severely disrupt the smoothness of the h-BN films. Here, we provide detailed characterization to the microstructure of h-BN wrinkles and demonstrate an effective post-synthesis smoothing route by thermal annealing under air. The smoothed h-BN film showed improved surface smoothness by up to 66 % and resulted in a much cleaner surface due to the elimination of polymer residues with no substantial oxidative damage to the film. The unwrinkling effect is attributed to the hydroxylation of the h-BN film as well as the substrate surface, resulting in a reduction in adhesion energy at the interface. Dehydroxylation occurs over time under ambient condition at room temperature and the smoothed film can be restored back with the intrinsic properties of h-BN. This work provides an efficient route to achieved smoother h-BN films which are beneficial for high-performance 2D heterostructure devices.

Introduction

Hexagonal boron nitride (h-BN) is one of the crucial building blocks for two-dimensional (2D) heterostructure devices owing to its unique electrically insulating nature, atomic smoothness and low density of surface dangling bonds.^{1–3} In order to achieve scalability for practical applications, various methods have been used to synthesize large-scale h-BN films. To date, the most utilized synthesis technique to fabricate such films is by using metal-catalyzed chemical vapor deposition (CVD).^{4–7} However, the h-BN films that are produced and their post-synthesis processes (i.e., the transfer process) often induce defects, strains, and contaminants. Recently, researchers have made significant progress in developing better quality h-BN films by growing larger-sized single crystals,^{8–10} grains with aligned orientation,^{11–13} achieved cleaner films by filtering/purifying the precursor,^{14,15} and enhancing the subsequent transfer process.^{16–19} However, attaining an atomically smooth surface is still greatly impeded by the presence of thermally-induced wrinkles. In particular, as h-BN is frequently used as an interfacing material, the increased surface roughness caused by wrinkling has remained a

widespread problem which significantly hampers the effective utilization of CVD-grown h-BN films.

Wrinkles are out-of-plane lattice distortions which are ubiquitous in 2D films such as graphene and h-BN, which are grown on metallic substrates, due to the presence of thermal stress between the film and the underlying growth substrate. Briefly, upon thermal quenching at high growth temperatures of 1000 °C and above, the large difference in coefficient of thermal expansion (CTE) between graphene or h-BN and the metal substrate (i.e., Cu and Ni) causes the metal to corrugate by step bunching due to tensile strain and the graphene or h-BN overlayer to form wrinkles due to compressive strains.^{20–25} Although wrinkles are usually detrimental as they result in uneven surfaces and alter the properties of the film,^{26,27} understanding its structure through in-depth characterization could lead to other creative and novel uses.^{28,29} However, in comparison to graphene, the wrinkling structure of h-BN and methods to reduce the surface roughness have not been extensively explored.

Here, we provide detailed characterization to the h-BN wrinkles formed during CVD growth on Cu foils and after transferring onto SiO₂/Si substrates. We further demonstrate an effective solution to smoothen the wrinkles and thus enabling smoother films. Efficient strain relaxation through corrugation of the Cu surface by step bunching is evident due to the large difference in CTE with the monolayer h-BN. When the h-BN film is transferred to a flat SiO₂ surface, the uneven corrugated structure is able to be released upon film detachment but wrinkles are still prevalent due to the excess h-BN along the Cu steps and terraces. These wrinkles, however, can be efficiently smoothened by simply annealing under air at 550 °C. During annealing, hydroxylation occur on both the h-BN film and SiO₂

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surfaces which caused a reduction in adhesion energy between the h-BN/SiO₂ interface and resulted in the unwrinkling of the h-BN film. Due to the high temperature stability of h-BN, negligible amount of oxidative damages to the film at temperatures below 840 °C was recorded. Dehydroxylation occurs over time and the h-BN film is subsequently restored back to its original state.

Experimental section

CVD Growth of NG

Cu foils (Nilaco, 25 µm thick) were used as growth substrates for the h-BN films. Prior to growth, the Cu foil was first dipped into dilute nitric acid for a few seconds and followed by rinsing with deionized (DI) water to remove away the coatings on the Cu surface. The Cu foil was then loaded into a 1 inch quartz tube under a constant Ar/H₂ flow of 200:20 sccm. The furnace was ramped up to 1050 °C in 40 min and kept constant for another 1 h to anneal the Cu and to remove the surface oxide. After annealing, 10 mg of ammonia borane complex (Sigma-Aldrich, product no. 682098, 97%) which was placed in a ceramic boat outside the heating zone was heated at ~85 °C to commence the film growth. The furnace was kept at 1050 °C for another 30 min for film growth and the lid of the furnace was lifted for quick cooling after growth.

Transfer Process

An electrochemical delamination process was used to transfer the h-BN films onto TEM grids, SiO₂/Si and quartz substrates. First, the as-grown h-BN film on Cu was spin coated with poly(methyl methacrylate) (PMMA) at 3000 rpm for 30 s. 1 M of NaOH was used as the electrolyte. A Pt foil was used as the anode and the spin-coated sample was used as the cathode. A constant voltage of 5–10 V was applied until the PMMA coated sample is completely detached from the Cu. The sample was then rinsed in DI water for several times and transferred onto a desired substrate. The as-transferred sample was baked at 80 °C until it is completely dried. Finally, the PMMA is removed by submerging the sample in acetone for several hours.

Thermal annealing

The transferred h-BN/SiO₂/Si samples were loaded into a 1 inch quartz tube with its ends exposed to ambient. The furnace was ramped up to the specified temperature at a rate of 50 °C/min and kept constant for 10 min. After annealing, the furnace was allowed to cool down and the samples were extracted out from the quartz tube at room temperature.

Characterization

Scanning electron microscopy (SEM, LEO 1550 Gemini) was used to observe the surface morphology of the wrinkles on the as-grown h-BN films on Cu substrates. Atomic force microscopy (AFM, Cypher scanning probe microscope) was done using tapping mode to characterize the surface of the h-BN films on Cu and SiO₂/Si substrates. Raman spectroscopy (Witec) with laser excitation wavelength of 532 nm was done at room temperature to determine the crystallinity of the transferred h-BN films on SiO₂/Si substrate. Transmission electron microscopy (TEM, JEOL 2100F) was operated with an acceleration voltage of 200 kV to determine the atomic

structure of the h-BN film. X-ray photoelectron spectroscopy (XPS, Thermo K-alpha) was used to determine the chemical bonding and elemental ratio of the transferred h-BN film on SiO₂/Si substrate. Ultraviolet-visible spectroscopy (UV-vis, Shimadzu UV-2450) was used to measure the absorbance spectra of the transferred h-BN film on quartz substrate. Fourier transform infrared spectroscopy (FTIR) analysis was conducted using an IRPrestige-21 spectrometer within wavelength range 4000–400 cm⁻¹. Goniometer (Dataphysics OCA 25) was used to measure the contact angles of DI water on the surfaces of transferred h-BN films, SiO₂/Si and quartz substrates under ambient condition. 0.5 µL deionized water droplet was released from a syringe needle onto the target surface and the image was captured using a CCD camera. The contact angle was measured by drawing a tangent line onto the contact point along the liquid-sample interface in the images.

Results and discussion

Fig. 1a shows an optical image of a continuous h-BN film transferred onto a 285 nm SiO₂/Si substrate with a distinctive Raman peak at 1371 cm⁻¹, corresponding to the E_{2g} vibration mode of monolayer h-BN.³⁰ High-resolution transmission electron microscopy (TEM) was utilized to determine the atomic structure of the film. **Fig. 1b** shows a TEM image of a suspended h-BN membrane over a TEM grid hole. Presence of partial folds and tears within the film can be observed as a result of the rough handling procedures used during the transfer process. The edges of the suspended membranes within the TEM grid were surveyed and most regions comprise of a single layer as shown in **Fig. 1c**. The crystalline structure within the interior of the membrane is consistent to that of h-BN which exhibits characteristic triangular-shaped defects due to the anisotropic etching by electron beam irradiation (**Fig. 1d**).³¹ Selected area electron diffraction (SAED) taken over the membrane shows a hexagonal pattern with measured d-spacings of 2.18 Å and 1.27 Å corresponding to the (10-10) and (21-10) planes of h-BN, respectively (inset of **Fig. 1d**), in good agreement with previous reported values.³²

Although the film may look smooth under an optical scope, atomic force microscopy (AFM) reveals the rough landscape of the h-BN film in the nano-scale (**Fig. 1e**). Excess surface area relative to a flat surface ($\Delta A/A_0$) represents the percentage increase of the three-dimensional surface area over the two-dimensional surface area, and provides a good measure of the surface roughness.³³ Many seemingly parallel lines with step heights ranging from ~1–4 nm can be observed throughout the scanned region with a periodicity (λ) of ~153 nm and a measured excess surface area relative to a flat surface ($\Delta A/A_0$) of ~0.12%. To identify the origin of these wrinkles, the as-grown h-BN film prior to transfer was carefully examined. **Fig. 1f** shows the AFM image of the highly-corrugated h-BN/Cu surface. Many uneven grooves with step heights ranging from ~3–18 nm and a similar λ of ~125 nm can be observed, demonstrating that the wrinkles observed in the transferred film are related to the morphology of the h-BN/Cu surface. However, the measured $\Delta A/A_0$ of the as-grown h-BN/Cu is ~2.55%, which is much larger than the transferred film. This huge disparity is attributed to the transfer process. In a typical transfer, the corrugated h-BN morphology is released during film detachment,³⁴ and upon transferring to a substrate, the film conforms to the flat SiO₂ surface with strong

Fig. 1 Characterization of wrinkles in monolayer h-BN films. (a) Optical image of transferred monolayer h-BN on SiO₂/Si substrate. Inset shows the corresponding Raman spectrum. (b) TEM image of a suspended h-BN membrane over a grid hole with several folded regions. High-resolution TEM images of (c) a folded edge and (d) interior of a monolayer h-BN. Inset in (d) show the corresponding SAED. (e) AFM image of the transferred h-BN in (a). (f) AFM and (g) SEM image of the as-grown h-BN film on Cu prior to transfer. (g) Schematic of the formation of wrinkles on monolayer h-BN film during thermal quenching. The red and green arrows indicate the contraction of bulk Cu and expansion of h-BN film, respectively.

adhesive energy by van der Waals forces.^{35,36} Hence, the effective excess h-BN surface area should reduce after transfer. It should be noted that different transfer processes will yield different degree of wrinkle density based on the duration of detachment process.

Fig. 1g shows a magnified scanning electron microscopy (SEM) image of the corresponding h-BN monolayer film on Cu. The periodic lines can be easily identified which are consistent over an individual Cu grain but may change over different grains in the polycrystalline Cu (**Fig. S1**, Supporting Information). This indicates that they are reconstructed Cu surfaces formed by step bunching,^{22,25} as a consequence of strain relaxation with an h-BN overlayer. The formation of the corrugated surface structure is further illustrated in the schematic in **Fig. 1g**. Similar to graphene, h-BN has an anisotropic thermal expansion behavior. The CTE of h-BN along the *c*-crystallographic axis, α_c , remained relatively constant at $\sim 40 \times 10^{-6} \text{ K}^{-1}$ in the range of 273–800 K, while it is negative along the in-plane direction, α_a , with measured values of $-2.8 \times 10^{-6} \text{ K}^{-1}$ at 293 K and $-0.9 \times 10^{-6} \text{ K}^{-1}$ at 800 K.³⁷ This indicates that the in-plane structure of the h-BN expands as temperature decreases. On the other hand, Cu has a positive CTE of $16.85 \times 10^{-6} \text{ K}^{-1}$ at 293 K and increases to $\sim 25 \times 10^{-6} \text{ K}^{-1}$ at 1300 K with an overall uniaxial expansion of 2.088% over the temperature range.³⁸ Hence, upon thermal quenching at the high growth temperature of 1050 °C, the in-plane structure of the h-BN expands while the bulk Cu contracts, causing strains along the h-BN/Cu interface. The Cu surface corrugates due to tensile stress by forming step bunches,^{22,25} while the excess h-BN form wrinkles by

mechanical deformation along more susceptible regions such as Cu step edges and Cu grain boundaries.²⁴ It should be noted that the corrugated Cu surfaces are independent of h-BN grain boundaries as they remained continuous over merged h-BN domains (**Fig. S2**, Supporting Information). Since the corrugated h-BN structures are released upon transfer, the wrinkles that are observed on the transferred h-BN originated from the excess h-BN which mechanically deformed over the Cu steps and hence, retained the similar periodic parallel lines.

It has been reported that unwrinkling in graphene by thermal annealing is accompanied by the formation of nanoscale pits and cracks as the result of oxidative etching.³⁹ This simple yet efficient technique, however, has not been extended to h-BN films, whose high-temperature and chemical stability make them resistant to oxidation at elevated temperatures of up to 850 °C for monolayers in air.^{40,41} For our CVD-grown h-BN films, we determined that they are thermally stable up to 840 °C before the onset of oxidation (**Fig. S3**, Supporting Information). Raman spectra showed broadening in the *E_g* peak when the film is annealed under air at 800 °C, which is attributable to reduced crystal size and increased defects.⁴² In contrast, negligible change to the Raman spectrum is observed at a lower annealing temperature of 550 °C, which indicates no oxidative damages to the film (**Fig. S4**, Supporting Information). To determine the temperature needed to smoothen the wrinkles, the as-transferred h-BN films on SiO₂/Si were respectively annealed at 350 °C, 450 °C, and 550 °C under air for 10 min. AFM imaging was used to

Fig. 2 Smoothing of wrinkles in transferred monolayer h-BN film. AFM images of a transferred monolayer h-BN film on SiO₂/Si substrate (a) before and after annealing under air for 10 min at (b) 350 °C, (c) 450 °C, (d) 550 °C, respectively. Their corresponding height profiles across the black lines are plotted below.

characterize the h-BN surface. The root-mean-square roughness (R_q) is a parameter obtained by calculating the standard deviation of the data within sampling area, which gives insights into height profile and surface uniformity.⁴³ **Fig. 2** shows the AFM images of the transferred monolayer h-BN film before and after thermal annealing at various temperatures. It is observed that the wrinkles could not be effectively smoothed at temperatures below 550 °C. However, when the film is annealed at 550 °C (or higher), most of the wrinkles were effectively smoothed with reduced height and width, resulting in a dramatic improvement in surface smoothness from a measured R_q of ~ 0.9 nm down to ~ 0.3 nm and a reduced $\Delta A/A_0$ from 0.19% down to 0.045%. No observable pinholes or cracks indicate that h-BN is indeed more resistant to oxidation as compared to graphene.

To probe the early stages of the smoothing process, we performed the same annealing procedure on the h-BN film with multilayers where there is higher density of wrinkles. **Fig. 3a–d** shows the AFM images of the as-transferred h-BN film and the same sample which subsequently underwent 10, 20 and 30 min of thermal

annealing at 550 °C under air. We observed a systematic decline in the height and width of the wrinkles with no oxidation-related etching to the film. The boxed regions indicate the measured surface roughness within the interior of an h-BN grain. Remarkably, most of the wrinkles have been eliminated after 30 min of annealing and the surface became very smooth (R_q of ~ 0.2 nm). It should be noted that the particles that are observed along the multilayer regions are carbonaceous contaminants from the environment due to prolonged annealing under air (**Fig. S5**, Supporting Information). Importantly, the presence of oxygen or other oxygen-containing molecules during the annealing is critical for the unwrinkling process as wrinkles are still prevalent even after 1 h of annealing under inert conditions (**Fig. S6**, Supporting Information).

X-ray photoelectron spectroscopy (XPS) was used to determine the chemical bonding and elemental compositions of the transferred h-BN film on SiO₂/Si substrate. **Fig. 4a–f** shows the high resolution B 1s, N 1s and C 1s spectra of the h-BN film before and after thermal annealing at 550 °C, respectively. It is observed that both samples displayed a single peak in the B 1s and N 1s core levels with a binding

Fig. 3 Smoothing of wrinkles in transferred h-BN film with multilayers. AFM images of a transferred h-BN film with multilayers on SiO₂/Si substrate (a) before and after annealing in air at 550 °C for (b) 10 min, (c) 20 min and (d) 30 min. Their corresponding height profiles across the black lines are plotted below.

Fig. 4 High-resolution XPS spectra of B 1s, N 1s and C 1s core levels for transferred h-BN film on SiO₂/Si substrate (a–c) before and (d–f) after annealing in air at 550 °C.

energy of around 191 eV and 398.3 eV, respectively, assigning to B–N bond.⁴⁴ The as-transferred h-BN film showed a relatively high amount of C composition of 59.8% with respect to B and N. Note that O was not included in the calculation due to presence of the underlying SiO₂ surface. Three deconvoluted peaks in the C 1s core level centering at 284.8, 286.3 and 288.2 eV, correspond to C–C/C=C, C–O and C=O bonds, respectively.⁴⁵ These are attributed to the residues and trapped absorbents by the PMMA,⁴⁶ which was used to coat the BN film during the transfer process. The C composition was significantly reduced to 39.7% for sample annealed at 350 °C and to ~32% for samples annealed at 450 °C and 550 °C, indicating that the majority of the PMMA impurities have been effectively removed.⁴⁶ This shows that a much cleaner h-BN surface can be obtained after

performing this simple annealing process.

Fourier transform infrared spectroscopy (FTIR) characterization, which is sensitive to oxygen-containing group, was performed on target surfaces to further investigate the role of oxygen in the unwrinkling of h-BN films by air annealing. The comparative FTIR spectra for Si substrates and h-BN/Si samples before and after air annealing are shown in **Fig. 5**. The transferred h-BN film can be detected as indicated by the characteristic peak at 1370 cm^{−1} which corresponds to the in-plane B–N stretching mode.^{47–49} Incorporation of hydroxyl group is evident on both bare Si and h-BN/Si samples after air annealing, as revealed by the new additional peaks at 3570 cm^{−1} and 3740 cm^{−1} which correspond to O–H stretching vibrational mode,^{50–55} confirming the presence of hydroxyl group on h-BN/Si

Fig. 5 FTIR spectra of (a, b) bare Si and (c, d) h-BN/Si samples before and after annealing in air at 550 °C for 10min, respectively.

Fig. 6 Surface functionalization of h-BN films. (a) UV-vis absorbance spectra and its corresponding (b) Tauc's plot of an as-transferred monolayer h-BN film (black trace), after annealing in air at 550 °C for 10 min (red trace) and after another week of inactivity under ambient conditions at room temperature (blue trace), on quartz substrate. CA of DI water droplets on (c) as-transferred monolayer h-BN film, (d) after annealing in air at 550 °C for 10 min and (e) after another week of inactivity under ambient conditions at room temperature, on SiO₂/Si substrate.

after air annealing.

To investigate the changes that occur in the h-BN film during and after the unwrinkling process, a fresh piece of monolayer h-BN film was transferred onto quartz substrate to examine its optical properties using ultraviolet-visible (UV-vis) spectroscopy. **Fig. 6a** shows the absorbance spectra of the monolayer h-BN film before and after thermal annealing at 550 °C for 10 min, and after an additional week under ambient conditions at room temperature, respectively. Their corresponding spectra are converted into Tauc's plots⁵⁶ in **Fig. 6b** for optical bandgap (OBG) extraction (**Fig. S7**, Supporting Information). Initially, the as-transferred h-BN film has an OBG of 6.1 eV, which is consistent with theorized value.⁵⁷ After annealing, the OBG decreased slightly to 5.985 eV, and subsequently recovered back to 6.085 eV after another week of inactivity under ambient conditions at room temperature. The temporal change in optical properties (i.e., lower OBG or broadening of absorption peak) is associated to the absorption of oxygen-containing functional groups such as hydroxyl groups during annealing under air, which modifies its surface chemistry.⁵⁸ After the annealing, as dehydroxylation take place over time,⁵⁹ the h-BN film recovered back to its intrinsic optical properties.

To further confirm this mechanism, contact angle (CA) measurements were done on the transferred h-BN film on SiO₂/Si following the same procedure. Initially, the as-transferred h-BN film exhibits a hydrophobic behaviour with a CA of ~100° (**Fig. 6c**). After annealing, the film surface became more hydrophilic and the CA dropped to ~40° (**Fig. 6d**). This trend of decreasing CA is consistent to a hydroxylated surface.^{59,60} After one week of resting under ambient conditions at room temperature, the CA partially recovered to ~65° (**Fig. 6e**). The increase in hydrophobicity is attributed to the

dissociation of the oxygen or hydroxyl groups due to the high resistivity of the h-BN film towards molecular oxygen, making it an energetically favorable process.^{59,61} On the other hand, the incomplete recovery of hydrophobicity of the film surface is because of the decreased in surface roughness of the unwrinkled film, where the measured CA is governed by:

$$\cos(\theta_w) = R_w \cos(\theta_0) \quad (1)$$

where θ_w is the measured CA, R_w is the surface roughness factor and θ_0 is the CA in Young's mode.⁶² Hence, the decreased in surface roughness of the h-BN film and removal of polymer residues resulted in an overall decreased in hydrophobicity. Additionally, the thermal annealing effects on bare SiO₂ and quartz surfaces were investigated. It is apparent that both the surfaces became more hydrophilic with increasing annealing temperature (**Fig. S8** and **Fig. S9**, Supporting Information), indicating the increase in oxygen intercalation at the surface.

Fig. 7 presents a schematic of the unwrinkling process. When transferred h-BN film on SiO₂/Si is exposed to air at 550 °C, oxygen and other oxygen-containing molecules from the air seep into the wrinkled h-BN/substrate interface through the edges of the transferred film or cracks induced by imperfect transfer. Upon thermal annealing, hydroxylation occur on both the h-BN film and the surface of the substrate. As the interaction between the h-BN film and the SiO₂ surface is dominated by van der Waals forces, the adhesion energy is effectively reduced when the surfaces are hydroxylated and further decreases with absorbed water molecules, resulting in a reduction in the equilibrium separation distance between the film and substrate.⁶³ Hence, the lifted h-BN wrinkle descends towards the hydroxylated SiO₂ surface over time.

Fig. 7 Schematic illustration of the smoothing process of transferred h-BN film when subjected to thermal annealing in air and its subsequent dissociation at room temperature.

After annealing, dehydroxylation occurs on both the unwrinkled h-BN film and SiO₂ surface.

Conclusions

In summary, the microstructure of wrinkles in CVD-grown h-BN films and their smoothing process by thermal annealing were investigated. The high density of wrinkles that are commonly observed in h-BN films are attributed to the large difference in CTE between h-BN and Cu which are formed upon thermal quenching. The Cu corrugates by step bunching while the excess h-BN form wrinkles and conforms to the corrugated structure as the consequence of strain relaxation. Although the corrugated h-BN/Cu structure can be released upon film detachment, the h-BN wrinkles prevailed after transferring to a relatively flat substrate such as SiO₂/Si. By simply annealing the transferred h-BN film under air at 550 °C, the wrinkles diminish over time with no observable oxidative detriment to the film. We concluded that the unwrinkling behavior is associated to the hydroxylation of the h-BN film as well as the substrate surface which resulted in a reduction in adhesion energy. When the unwrinkled film is brought to rest under ambient conditions at room temperature, dehydroxylation occurs over time and the film is restored back to its originally unmodified state. This work provides important insights into the microstructure of wrinkles in CVD-grown h-BN films and demonstrates an effective post-synthesis treatment to obtain smoother and cleaner films which is critical for the fabrication of scalable 2D heterostructure devices.

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Conflicts of interest

There are no conflicts of interest to declare.

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TOC graphic:

Supporting Information

Smoothing of wrinkles in CVD-grown hexagonal boron nitride films

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Fig. S1 (a) SEM image of as-grown h-BN film on Cu. (b,c) Magnified SEM images in (a) showing the different orientation of the step bunches on different Cu grains.

Fig. S2 (a) SEM image of a partially continuous monolayer h-BN film. (b–d) Magnified SEM images revealing the Cu corrugation across multiple h-BN grain boundaries.

Fig. S3 (a) Optical and (b) AFM images of transferred h-BN film after annealing at 840 °C for 2 h. The onset of oxidation can be observed by the presences of nanoscale pits and the elongated etch lines along the wrinkled structures.¹

Fig. S4 Optical images of (a) as-transferred h-BN film on SiO₂/Si substrate and after annealing in air at (b) 550 °C, (c) 800 °C and (d) 840 °C. (e,f) Raman spectra and their corresponding fitted peaks of the respective h-BN films in (a – d).

Fig. S5 Representative Raman spectrum in some regions of the annealed h-BN film with multilayers indicating the presence of carbonaceous contamination by the presence of D and G bands.

Fig. S6 AFM images of (a) as-transferred h-BN film and after annealing at 550 °C under 200:20 sccm of Ar/H₂ for (b) 10 min and (c) 1 h. The h-BN wrinkles are still prevalent even after 1 h of annealing in Ar and H₂.

Fig. S7 (a) UV-vis absorbance spectra and its corresponding (b) Tauc's plot of an as-transferred monolayer h-BN film (black trace), after annealing in air at 550 °C for 10 min (red trace) and after another week of inactivity (blue trace), on quartz substrate.

To convert the absorbance spectra into Tauc's plots for bandgap extraction, we use the derived formula for a direct band gap semiconductor,²

$$\alpha = C(E - E_g)^{1/2}/E \quad (1)$$

Where α is the absorption coefficient, C is a constant and E is the photon energy. α is calculated by the measured optical absorption divided by the film thickness. By plotting $(\alpha E)^2$ against E , a straight line can be extrapolated from the energy dispersion curves and their bandgaps, E_g , can be extracted at the intersection of the extrapolated lines and the x-axis.

Fig. S8 CA of DI water droplets on SiO_2/Si substrate (a) before and after annealing in air for 10 min at (b) 250°C , (c) 350°C , (d) 450°C , (e) 550°C , respectively.

Fig. S9 CA of DI water droplets on quartz substrates (a) before and (b) after annealing in air at 550 °C for 10min.

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