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Direct growth of nanocrystalline hexagonal boron nitride films on dielectric substrates

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Atomically thin hexagonal-boron nitride (h-BN) films are primarily synthesized through chemical vapor deposition (CVD) on various catalytic transition metal substrates. In this work, a single-step metal-catalyst-free approach to obtain few- to multi-layer nanocrystalline h-BN (NCBN) directly on amorphous SiO2/Si and quartz substrates is demonstrated. The as-grown thin films are continuous and smooth with no observable pinholes or wrinkles across the entire deposited substrate as inspected using optical and atomic force microscopy. The starting layers of NCBN orient itself parallel to the substrate, initiating the growth of the textured thin film. Formation of NCBN is due to the random and uncontrolled nucleation of h-BN on the dielectric substrate surface with no epitaxial relation, unlike on metal surfaces. The crystallite size is ~25 nm as determined by Raman spectroscopy. Transmission electron microscopy shows that the NCBN formed sheets of multi-stacked layers with controllable thickness from ~2 to 25 nm. The absence of transfer process in this technique avoids any additional degradation, such as wrinkles, tears or folding and residues on the film which are detrimental to device performance. This work provides a wider perspective of CVD-grown h-BN and presents a viable route towards large-scale manufacturing of h-BN substrates and for coating applications. © 2015 AIP Publishing LLC.

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Two-dimensional (2D) hexagonal boron nitride (h-BN; referred to BN hereafter) is exceptionally fascinating owing to its extremely attractive properties and compatibility with graphene.1,2 2D BN’s synthesis methodology has thus received a lot of attention in recent times.3–5 While exfoliation produces the best quality 2D BN with high crystallinity and very smooth surfaces (root-mean-square (RMS) roughness of ~100 pm),1 its reliability to generate consistent large domain size with controllable thickness is poor. Moreover, this technique is simply not viable for large-scale integration into current electronics devices and applications. Recently, high quality large area mono- to few-layer 2D BN films were synthesized on a variety of transition metals such as Cu, Ni, and Pt substrates by chemical vapor deposition (CVD) using ammonia borane (NH3BH3) as the precursor.3–6 This CVD approach thus opens up a potentially industry acceptable technique as it adopts a similar paradigm to large area thin film deposition methodology. However, the metallic substrates, especially Cu, require extensive pre-treatments such as electrochemical polishing (ECP) or chemical mechanical polishing (CMP) to smoothen the rough surfaces. Rigorous annealing times are also needed to expand their grain sizes to further smoothen their substrate prior to deposition. In addition, after growth, the BN film would still require a separate lift-off process7 to transfer the film onto a more useful dielectric substrate such as SiO2 for subsequent patterning and device fabrication. Therefore, a direct growth approach with no transfer processes both mitigates the damages done to the film (due to the lift-off processes) and is much more scalable for direct integration into future Si-based processes. However, less work was conducted on the growth of 2D BN using a catalyst-free process and its formation mechanism.8

In this letter, we demonstrate a metal-catalyst-free and direct growth of large area nanocrystalline BN (NCBN) films on amorphous SiO2 and quartz substrates with controllable thickness. This technique is a substrate independent process, where the variety of substrates that can be used is only limited to the thermal stability of the material to withstand the high growth temperature.

The growth is carried out using a split tube furnace with a fused quartz processing tube (25 mm diameter), similar to previous reported setup.9,10 Prior to deposition, the 285 nm SiO2/ Si substrates were cleaned by ultrasonication in acetone and followed by isopropyl alcohol (IPA) for 10 min, respectively. The furnace was then ramped up to 1000 °C under a constant flow of 500 sccm of Ar and 20 sccm of H2 at a pressure of 1.1 Torr (atmospheric pressure can also be used). Upon reaching 1000 °C, 30 mg of ammonia borane (NH3BH3), purchased

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from Sigma Aldrich, was sublimed at ~100 °C and the reaction was carried out for 5–30 min. The process is the same for the growth on quartz substrates. Finally, the lid of the furnace is lifted for fast cooling. In contrast to recent BN growth procedure, no Cu or any other metal catalyst was used during the growth process. Importantly, all the quartz tubes that were used were brand new with no Cu contaminants. This precludes any Cu residues that may become “accidental catalytic agents.” The complete exclusion of Cu is important as we want to demonstrate clearly that there are no additional collisions from any potential floating residual Cu atoms which might aid the dissociation of the precursor.11

The growth mechanism of NCBN can be explained by considering the chemical decomposition and the reaction kinetics during the CVD growth process. Ammonia borane (BH₃NH₃) is initially broken down into aminoborane (BH₂NH₂) and subsequently borazine (B₃H₆N₃) when heated beyond 60 °C.12 The decomposed products are then transported towards the substrate surface where borazine undergoes further dehydrogenation at ~1000 °C.13,14 where it is directly converted into active molecules consisting of (BH₄)ₓ and (NH₃)ₓ (1.2 < x < 2.4).14 The decomposition rate of borazine can be expressed through Arrhenius equation r = A* exp(−Ea/RT),15 where r is the reaction rate, A is the pre-exponential (“frequency”) factor, Eₐ is the activation energy, R is the universal gas constant, and T is the absolute temperature. For BN film growth, a sustainable r must be retained. With r being largely affected by the interplay between the T and Eₐ, a balance between these two parameters is crucial. For typical CVD growth of BN using metallic substrates, the presence of the catalyst would lower Eₐ and as such a lower T would be possible. In contrast, during direct deposition where catalytic metals are absent, the reaction barrier is expected to be higher (hence higher Eₐ). In order to surmount this increased energy barrier, our process needs T exceeding 900 °C to compensate for the increased in Eₐ. This is in contrast to the lowest recorded BN growth at 750 °C grown using Cu substrates.16 A crucial point here is the high thermal stability of BN (higher than 1000 °C),17 which allows for the (BH₄)ₓ molecules to be directly deposited onto the surface of the substrate, leading to BN growth.

Fig. 1(a) shows a schematic representation and a photograph of large area as-grown BN films on SiO₂/Si substrates. The BN films fully cover the substrates and have a slightly blue appearance after being deposited on 285 nm SiO₂/Si substrates. The optical image in Fig. 1(b) presents a scratched region of the as-grown film exposing the underlying SiO₂ surface. XPS survey (Fig. 1(c)) and magnified XPS spectra for Cu 2p, B 1s, and N 1s, respectively. The peak binding energies for N 1s and B 1s are 398.4 eV and 190.7 eV, respectively.

FIG. 1. (a) Schematic diagram (top) and photograph (bottom) of direct-grown NCBN films on SiO₂/Si substrates. (b) Optical image of as-grown NCBN film with a scratched region exposing the underlying SiO₂ surface. (c) XPS survey and magnified XPS spectra of (d) Cu 2p, (e) B 1s, and (f) N 1s, respectively. The peak binding energies for N 1s and B 1s are 398.4 eV and 190.7 eV, respectively.

which is very close to theoretical value of 1:1 B/N stoichiometry in BN films.

As the growth of BN is known to have non-self-limiting growth mechanisms,9 the direct growth of NCBN was varied from 5 to 30 min. Figs. 2(a)–2(d) show the optical images with its corresponding atomic force microscopy (AFM) images of the SiO₂ surface and the as-grown NCBN films grown for 5 min (sample #1), 10 min (sample #2), and 30 min (sample #3), respectively. The optical images, which were taken under the same illumination settings, showed a clear color contrast between the different growth times and evidenced the presence of thicker films with increasing growth duration. AFM measurements with scanned area of 5 × 5 μm² showed that the surface morphology of the film increases in RMS roughness, R₟, from 0.24 nm for sample #1 to 0.45 nm for sample #3, indicating an increase in surface irregularities as the film grows thicker.

Raman spectra using WITec Raman spectroscopy with laser excitation wavelength of 532 nm were collected in Fig. 3(a) to determine the quality of the BN films. The fitted Raman spectra for sample #1, sample #2, and sample #3 are shown in Figs. 3(b), 3(c), and 3(d), respectively. The fitted results are tabulated in Table I. A single peak located at ~1371 cm⁻¹ is observed on the NCBN films corresponding to the E₂g vibration mode of BN.19 and the smaller band at 1450 cm⁻¹ is assigned to the third order Si transverse optical (TO) phonon which is present due to the underlying SiO₂/Si
Due to the thicker films in samples #2 and #3 as compared to sample #1, the intensities of the Raman signals are significantly higher. The extracted full width at half maximum (FWHM) of the NCBN films ranges between 42 and 46 cm$^{-1}$. These values are significantly larger than an exfoliated monolayer BN flake and CVD-grown BN on catalytic metal substrates (FWHM of ~20 cm$^{-1}$). The notable broadening of the FWHM is attributed to the presence of smaller crystallite sizes of the NCBN film due to the uncontrolled and random nucleation on the SiO$_2$ surface. The domain size can be calculated using $L_d = \frac{1417}{\Gamma_{1/2}} - 8.7$, where $L_d$ is the domain size and $\Gamma_{1/2}$ is FWHM of the Raman peak. The extracted $L_d$ for samples #1–#3 varies slightly between 23.0 and 24.9 nm.

To determine the thickness and microstructure of the NCBN films, samples #1 and #3 were transferred onto a transmission electron microscope (TEM) grid and TEM analysis was carried out using JEOL 2010 operated with an acceleration voltage of 200 kV. Figs. 4(a) and 4(b) show a representative cross-section TEM image taken at the film edge of samples #1 and #3, respectively. The interlayer distance on both films is ~0.35 nm which matches the previous reported value and a measured thickness of ~2.45 nm (7 layers) for sample #1 and ~17.5 nm (50 layers) for sample #3. The NCBN layers are clearly oriented parallel to the substrate leading to well-aligned stacked 2D sheets bonded by weak van der Waals forces.

To measure the optical bandgap (OOG) of the material (and also to demonstrate the substrate independent nature of our process), two separate growths were done using the growth conditions from sample #1 (5 min growth time) and sample #3 (30 min growth time) on quartz substrates. Ultraviolet-visible (UV-vis) spectroscopy (Shimadzu UV-2450) was used to measure the optical properties of the NCBN films. Figs. 4(c) and 4(d) show the absorbance spectrum of the NCBN films on quartz substrates which were grown for 5 min and 30 min, respectively. Both films are highly transparent with a sharp

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**TABLE I. Tabulated Raman measurements of NCBN films.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (nm)</th>
<th>Center (cm$^{-1}$)</th>
<th>FWHM (cm$^{-1}$)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
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<td>#1</td>
<td>2–4</td>
<td>1370.79</td>
<td>45.63</td>
<td>23.0</td>
</tr>
<tr>
<td>#2</td>
<td>4–8</td>
<td>1371.55</td>
<td>42.14</td>
<td>24.9</td>
</tr>
<tr>
<td>#3</td>
<td>15–25</td>
<td>1371.20</td>
<td>42.14</td>
<td>24.9</td>
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**Fig. 2.** Optical (top panel), AFM (bottom panel) images of (a) SiO$_2$ substrate and as-grown NCBN films grown for (b) 5 min, (c) 10 min, and (d) 30 min. The optical images were taken using the same illumination settings for comparisons. RMS roughness, $R_q$, was extracted from each of the AFM images within a 5 $\mu$m $\times$ 5 $\mu$m scanned region.

**Fig. 3.** (a) Raman spectra of SiO$_2$ and as-grown NCBN films grown for 5 min (sample #1), 10 min (sample #2), and 30 min (sample #3) directly on SiO$_2$/Si substrate. Fitted Raman spectrum for (b) sample #1, (c) sample #2, and (d) sample #3.
absorption peak at \( \sim 202 \) nm. To calculate the OBG, the absorption spectrum is converted to Tauc’s plot using the derived absorption coefficient for a direct bandgap material, which is defined as \( \alpha = C(E - E_g)^{1/2}/E \), where \( \alpha \) is the measured absorbance and \( E \) is the photon energy. Hence, by plotting \( (\alpha E)^{2} \) against \( E \), a linear graph to extract \( E_g \) can be obtained. Figs. 4(e) and 4(f) show the corresponding Tauc’s plot \( (\alpha E)^{2} \) vs. \( E \), with an extrapolated line intersecting the \( x \)-axis can be obtained. The bandgap increases, the bandgap reduces to \( 5.59 \) eV due to the increased interlayer distance. However, it is still significantly larger than bulk BN of \( \sim 5.2 \) eV.

The electronic property of the as-grown NCBN layers was further characterized by using a four-point probe technique. Figure 5(a) shows a NCBN device fabricated using a two-step photolithography process. The film was first patterned to retain a 40 \( \mu \)m \( \times \) 10 \( \mu \)m for measurements, and the undesired area was etched away using oxygen plasma. The contact pads were deposited using electron beam evaporated 5 nm/50 nm Ti/Au layers which were subsequently defined after a standard lift-off technique. The distance between each electrode is \( \sim 4 \) \( \mu \)m. Electrical measurement was conducted at room temperature and at ambient conditions using Keithley 4200 semiconductor characterization system. Fig. 5(b) shows the 1-V measurement of the device. No current is observed in the NCBN film, indicating that the film is electrically non-conducting and further confirming its insulating property which is expected of a wide bandgap dielectric material.

**In summary**, few- to multi-layer NCBN were directly grown on amorphous SiO\(_2\)/Si and quartz substrates without the aid of any metal catalyst. At \( \sim 1000 \) °C, borazine undergoes a further dehydrogenation path converting it directly into (BNH\(_2\))\(_x\) molecules, enabling it to be deposited onto any substrate. Due to the non-self-limiting growth mechanism, the thickness of NCBN can be easily controlled by using different growth time. The starting BN layers initially grow parallel to the SiO\(_2\) surface and thicken over time as more precursor gas (borazine) was supplied into the reaction. As the film grew thicker, it roughened due to surface irregularities and along the multiple grain boundaries. The crystallite sizes are extracted to be \( \sim 23.0\)–\(24.9\) nm. The NCBN films retained a highly insulating property with a wide bandgap ranging from \( 5.59 \) eV for thicker films of \( \sim 17.5 \) nm and \( 6.03 \) eV for atomically thin films of \( \sim 2.45 \) nm. The transfer-free process allows easy integration towards large-scale manufacturing of BN with compatible Si-based technology and opens up other applications for thermally and chemically stable ultrathin non-conductive coatings.

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