Chemical Vapour Deposition of Hexagonal Boron Nitride for Two Dimensional Electronics

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Abstract

Hexagonal boron nitride (h-BN) has potential applications in protective coatings, single photon emitters and as substrate for graphene electronics. In this paper, we report on the growth of h-BN by chemical vapor deposition (CVD) using ammonia borane as the precursor. Use of CVD allows controlled synthesis over large areas defined by process parameters, e.g. temperature, time, process chamber pressure and gas partial pressures. Furthermore, independently grown graphene and h-BN layers are put together to realize enhancement in electronic properties of graphene.

Author Keywords. Hexagonal Boron Nitride, Chemical Vapor Deposition, Ammonia borane, Graphene Electronics

1. Introduction

Two dimensional (2D) materials such as graphene and hexagonal boron nitride (h-BN) have attracted scientific and technological interest for potential applications in next generation electronics. The interest is increased since chemical vapor (CVD) synthesis of these 2D materials on large areas was demonstrated (Mattevi, Kim, and Chhowalla 2011). Hexagonal boron nitride (h-BN) is an electrical insulator that can be regarded as the dielectric equivalent of graphene, in the sense that both materials have 2D honeycomb lattices that are commensurate (Kim et al. 2012; Xu et al. 2013). In addition to insulating properties, h-BN has high chemical resistance, high thermal stability, low dielectric constant, high mechanical strength and high corrosion resistance leading to potential applications (Meric et al. 2013; Kubota et al. 2007). These properties translate into attractive applications like substrate for graphene electronics, single photon emitters, charge leakage barriers and lubricants (Song et al. 2010).

Boron nitride (BN) occurs in many allotropic forms, from amorphous thin films (a-BN) analogous to amorphous carbon, to the hexagonal 2D form, which is the most stable of all, and is generally referred to as h-BN. The form analogous to diamond has a cubic lattice, referred to as c-BN, and has thermal and chemical characteristics superior to diamond, though it is much softer than diamond (Wentorf 1957). There is also a rare wurtzite form of boron nitride (w-BN) equivalent to carbon lonsdaleite (hexagonal diamond), where crystal structure is more compact, with a hexagonal unit cell rather than a tetragonal one (Silberberg 2009). The h-BN belongs to point group =D_{6h}; space group = $P6_3/mmc$ having a layered structure with in-plane covalently bonded boron and nitrogen atoms and these layers are held together by weak van der Waal forces. Single crystal basal plane in h-BN is not easily broken because of its strong in-plane bonds. Also, in contrast to graphite which displays AB Bernal stacking, h-BN stacks exhibit AA´ sequences (Kawaguchi, Kuroda, and Muramatsu 2008).

h-BN is an excellent platform for graphene electronics. A conventional dielectric such as SiO_2 can host impurities, surface roughness and charged surface states, degrading the transport properties of graphene. Whilst h-BN benefits due to atomically smooth surface and free of adsorbed impurities. Dean et al. (2010) investigated the use of h-BN as supporting substrate for graphene which resulted in a 3-4 fold increase of carrier mobility. Several other groups (Wang et al. 2011; Gannett et al. 2011; Meric et al. 2013) reported similar enhancement of graphene transport properties using h-BN as a dielectric substrate instead of SiO_2. Numerical calculation of thermal conductivity using phonon Boltzmann transport equation is reported as 600 W/m K (Lindsay and Broido 2011). Experimental thermal conductivity on h-BN is reported to be 360 W/m K at room temperature which is many times higher than that of SiO_2 making it a better candidate as the dielectric material for heat generating electronics (Jo et al. 2013). All of these studies employed, h-BN flakes exfoliated from h-BN crystals thus limiting technological use of these films. Hence, there is an urgent need to develop an alternative approach to prepare large-scale and high-quality h-BN for present and future applications. CVD presents itself as the most relevant alternative. Moreover, it is already used for the growth of other 2D materials. Yet, precise layer number control and growth conditions are still uncertain. Studies reported in Kim et al. (2012), Ismach et al. (2012) and Lee et al. (2012) does not ascertain precise deposition parameters and sublimating conditions. Here, we present a route for growth of hexagonal boron nitride (h-BN) by CVD using ammonia-borane ($H_3N\text{-}BH_3$) as the BN precursor with precise details of sublimation conditions.

2. Materials and methods

The CVD system (First Nano ET3000) consists of a cylindrical quartz process tube of 5" outer diameter that can accommodate samples measuring up to 10 cm × 15 cm. It has a load lock chamber with transfer arm for loading/unloading samples. Temperature is cascade controlled up to 1200°C within the three zone resistively heated furnace. Unlike crude models of CVD where solid precursor is placed inside main process tube, ET3000 has a dedicated remote solid source reservoir connected to the process tube by a heated ¼"stainless steel tubing. The sublimating temperatures are applied directly to the reservoir body and top, and can be ramped for desired heating rates.

Ammonia borane (AB) (H3BNH3, also called borazane) is non-flammable and non-explosive under ambient conditions. AB has 1:1 B:N stoichiometry which favors the formation of h-BN. AB is chosen instead of borazine, because of its stability in ambient atmosphere whereas Borazine in presence of moisture hydrolyzes to boric acid, ammonia and hydrogen. The method primarily relies on sublimating ammonia borane at 100 C which is then carried into

the process tube by carrier gas H_2. We have grown thin films of h-BN on Cu by sublimating at temperatures from 40 °C to 100 °C. Growth lasts for one hour at 2 Torr pressure and 1000 °C temperature. A 4:1 mixture of Ar:H_2 with flow rates of 200:50 sccm is used as a carrier gas to transport precursor vapor to chamber.

Raman spectra were acquired at room temperature in backscatter geometry using a WiTec Alpha 300 equipped with a 532 nm frequency-doubled Nd-YAG laser. Data is collected with 600 g/mm or 1800 g/mm gratings at 50× magnifying objective lens for a laser power level ~10mW. The E_{2g} band position is at ~1370 cm^{-1}. Acquisition time was between 10 and 20 s. Raman of h-BN on Cu did not yield any visible signal due to reflection by the Cu background. Hence the Raman spectra measurements were performed on h-BN films transferred onto Si/SiO_2 substrates.

3. Results and discussions

The as-grown h-BN layers were characterized by Raman spectroscopy which confirms the E_{2g} peak in Figure 1b at ~1369 cm^{-1} corresponding to monolayer hexagonal boron nitride. Raman mapping shown in Figure 1a taken at (20x20) different points in a (200x200) μm^2 area shows a continuous h-BN over whole area. Raman intensity changes at different locations corresponding to thickness variation, but E_{2g} peak is constant indicating continuous film. In agreement with literature, peak position is thickness dependent, where monolayer ranges from 1367 to 1370 cm^{-1} and bi layer ranges from 1363 to 1365 cm^{-1} (Gorbachev et al. 2011).
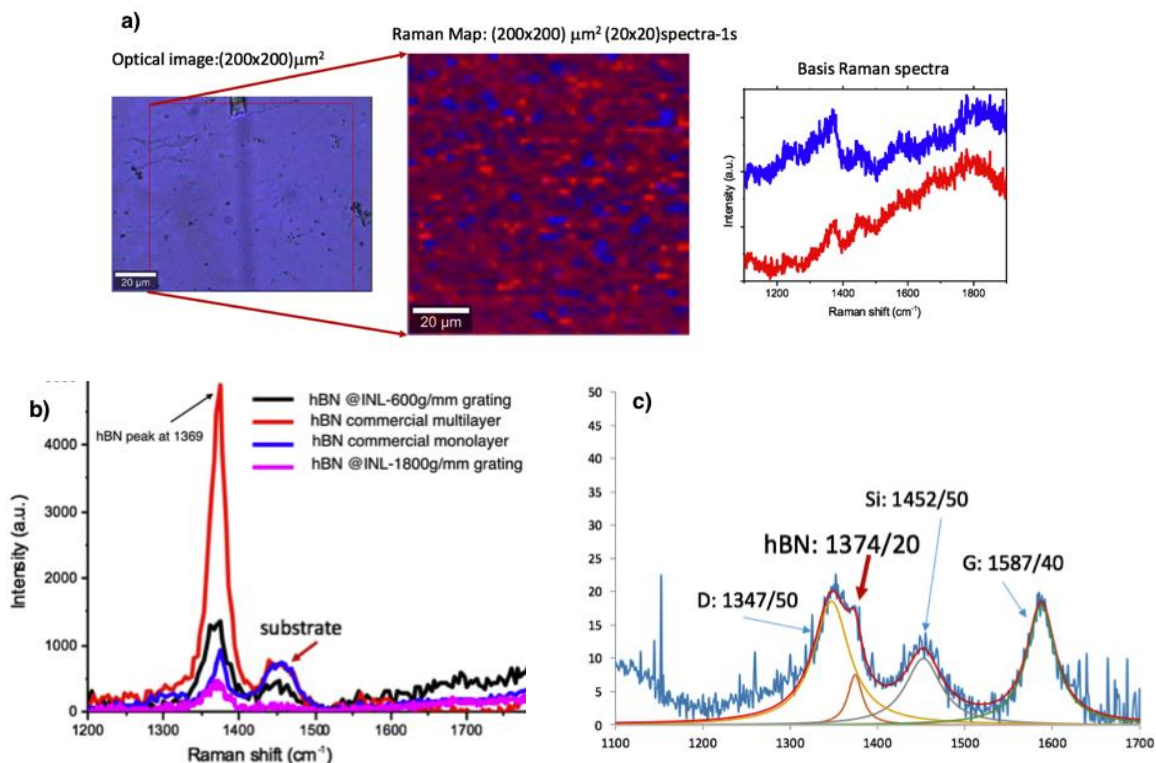
Figure 1: a) h-BN coverage post transfer to Si/SiO_2 b) Raman peak at ~1369 cm^{-1} identifying monolayer h-BN c) Raman of graphene / h-BN stacked layer showing peak assignment: position/FWHM

AFM images were collected using Bruker dimension icon in tapping mode with tapping frequency of ~100 KHz and a scan rate of 0.5 Hz with sampling of 256x256 pixels and scan area of 40 square microns. Images were analyzed using Image SXM 200 software. It is clear that surface corrugations are much large on SiO_2 compared to h-BN. This agrees with the planar nature of h-BN as compared to amorphous SiO_2. Root mean square roughness measured for bare SiO_2 is 11.3 ± 0.5 nm and for h-BN on SiO_2 is 6.1 ± 0.5 nm. As shown in Figure 2, hexagonal

boron nitride is atomically very smooth when compared to SiO₂. Results are in agreement with previously reported values (Xue et al. 2011). Thickness of monolayer measured using AFM scan and was found to be 0.4 nm. This is closely in agreement with thickness observation of 0.33 nm in literature (Golla et al. 2013).
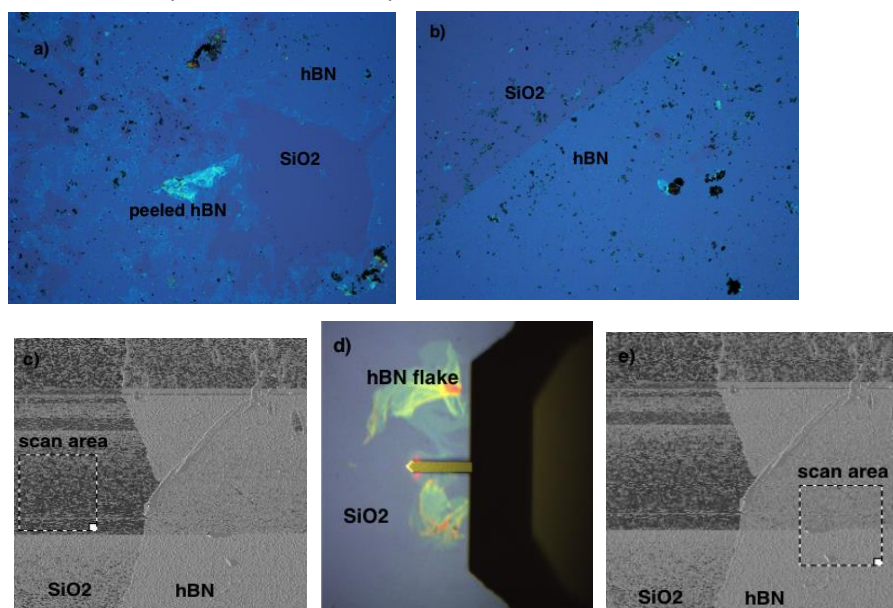
Figure 2: a) Optical image of h-BN peeled off on Si/SiO2 b) Optical image of hBN on Si/SiO2 edge c,e) AFM roughness scan of hBN and Si/SiO2

3.1. Growth of h-BN on copper

It has been reported that h-BN monolayers readily grow with hexagonal structure of transition metal catalysts such as, Cu, Ni, Pt, in (111) direction. Preobrajenski, Vinogradov, and Mårtensson (2005) showed that h-BN film on Cu (111) has a commensurate structure, which is stable when N atoms are bound directly over Cu atoms and B atoms over FCC hollow sites resulting in a film under slightly compressive stress. As shown in the Table 1, Laskowski, Blaha, and Schwarz (2008) reported binding energies of h-BN on different transition metals through density functional theory (DFT) calculations. Metals with high binding energy and large lattice mismatches, greater than 10%, like Pt and Ir, can cause Nano mesh-like film structure due to strong straining of h-BN σ bonds (Preobrajenski, Vinogradov, and Mårtensson 2005).

High binding energy with good lattice match to the metal catalyzer should be considered when choosing a suitable substrate for h-BN deposition. Ni and Cu having a lattice mismatch of 0.4% and 0.9%, respectively, are considered ideal for synthesizing commensurate h-BN layers (Joshi et al. 2012). h-BN layers on Ni foils are considered leakier as dielectric layer due to incomplete regions present at Ni grain boundaries (Bresnehan et al. 2014). Hence, growth on Cu foils is realistic and suitable for upscaling. For dielectric applications the tunneling currents were found to be excessive for h-BN films less than four layers thick (Britnell et al. 2012).

Element	ΔE (Binding energy by LDA)
Co	0.32
Ni	0.27
Cu	0.19
Ir	0.49
Pt	0.34
Au	0.16
Ag	0.19

Table 1: Binding energies of h-BN on different transition metals. Reprinted table with permission with Laskowski, Blaha, and Schwarz (2008)

3.2. Sublimation of AB

The results show enhanced dehydrogenation of AB at 80 °C only after it was pre-heated at the same temperature for four hours. Thermal treatments of AB were performed in the same reservoir with dummy runs. With increased pre heating duration the dehydrogenation is faster and effective. This was also realized by the group of (Zhang et al. 2010) for the study of AB as solid source of hydrogen fuel. During the preheating stage the solid AB is decomposed to diammoniate of diborane (DADB, $[(NH_3)_2BH_2]^+[BH_4]^-$) and few other polymeric and oligomeric species of BH_2N_2. This reaction shifts the melting point of AB to a lower value (Stowe et al. 2007). After the pre-heating stage h-BN growth is rapid. An understanding of this incubation period of AB allows for a significant reduction in h-BN growth time and a greater control over the process.

At low sublimating temperatures, the ammonia borane precursors are not fully evaporated. Series of runs with every 5 °C raise in temperature were performed. High quality films with good substrate coverage were achieved at sublimating temperatures of 100 °C. Thermal decomposition of AB takes place in several weight loss steps releasing H_2 and BN complexes. Starting with an endothermic process at 101 °C, resulting in the melting of AB, followed by exothermic decomposition steps at ~110, ~130 and 1170 °C. The first weight loss at 110 °C releases H_2 and monomeric amino borane (BH_2NH_2) with residual solid polyaminoborane. Second weight loss step at 130 °C results in further hydrogen release along with borazine ($B_3N_3H_6$). Finally, at 1170 °C hydrogen is fully released, resulting in the formation of crystalline hexagonal boron nitride phase (Frueh et al. 2011).

3.3. Graphene/h-BN hetero-structure

Graphene was transferred onto h-BN/Si/SiO2 substrates using Cu etch method. For that, the as-grown h-BN films have to be first decoupled from the native Cu substrate and then transferred onto Si/SiO_2 wafers, using a temporary, polymeric substrate (poly-methyl-methacrylate, PMMA). Post transfer the samples were annealed for 12 hours at 150 °C and the process is repeated to transfer graphene. The resulting Graphene/h-BN heterostructure was measured for Raman signature. The Raman spectrum shown in Figure 1c shows prominent G-line centered at 1587 cm^{-1} and Full-width at half maximum (FWHM) 49 cm^{-1}, as expected for graphene. The peak centered at 1374 cm^{-1} (FWHM = 20 cm^{-1}) can be attributed to Raman active LO-phonon in h-BN. It is crucial to distinguish this peak from defect induced D-line in graphene, appearing around 1347 cm^{-1} (FWHM = 50 cm^{-1}). Study by optical microscopy shows presence of impurities accumulated during the transfer. It is challenging to prevent adsorption of water molecules and other chemicals at the interface during the transfer. Due to these fundamental challenges graphene grown over h-BN film will exhibit better performance as the interface is protected from external impurities. Extensive characterization revealed a stable heterostructure which can be further patterned to make devices, e.g. a field effect transistor.

4. Conclusions

In this work, we successfully synthesized large area h-BN films using low pressure CVD. The results shown above support past observations in the literature and detail additional mechanistic insight into the elementary process that lead to pristine h-BN films by thermal decomposition of solid AB. The layers were characterized using Optical microscopy, Raman spectroscopy and AFM. The thickness of monolayer was found to be 0.4nm.

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