

Rapid and catalyst-free van der Waals epitaxy of graphene on hexagonal boron nitride



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ABSTRACT

Recently, hexagonal boron nitride (h-BN) has been shown to act as an ideal substrate to graphene by greatly improving the material transport properties thanks to its atomically flat surface, low interlayer electronic coupling and almost perfect reticular matching [1]. Chemical vapour deposition (CVD) is presently considered the most scalable approach to grow graphene directly on h-BN. However, for the catalyst-free approach, poor control over the shape and crystallinity of the graphene grains and low growth rates are typically reported [2–5]. In this work we investigate the crystallinity of differently shaped grains and identify a path towards a real van der Waals epitaxy of graphene on h-BN by adopting a catalyst-free CVD process. We demonstrate the polycrystalline nature of circular-shaped pads and attribute the stemming of different oriented grains to airborne contamination of the h-BN flakes. We show that single-crystal grains with six-fold symmetry can be obtained by adopting high hydrogen partial pressures during growth. Notably, growth rates as high as 100 nm/min are obtained by optimizing growth temperature and pressure. The possibility of synthesizing single-crystal graphene on h-BN with appreciable growth rates by adopting a simple CVD approach is a step towards an increased accessibility of this promising van der Waals heterostructure.

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1. Introduction

Hexagonal boron nitride (h-BN) is a two-dimensional (2D) large-bandgap insulator constituted of alternating boron and nitrogen atoms disposed in a honeycomb structure. It shares with graphene a high thermal stability and chemical inertness, an atomically-smooth surface and an almost matching lattice constant (1.7% mismatch). Often referred to as “white graphene”, it has recently been proposed as the ideal platform for developing next generation graphene electronics. Indeed, its reticular match with graphene and low interlayer electronic coupling have been shown to significantly improve graphene mobility and carrier homogeneities [1]. Vertical heterostructures of graphene and h-BN alternating layers have been used to implement tunnelling field effect transistors (TFETs) with remarkable on-off ratios [6] and, more recently, TFETs with resonant tunnelling – potentially appealing for

high-frequency applications [7].

In order to move towards a more scalable approach, which might potentially lead to the large scale implementation of novel electronic devices with superior performances, several groups have attempted to grow graphene directly on h-BN substrates, mostly by adopting chemical vapour deposition (CVD) approaches [2–5,8–13]. To date, the difficulty in obtaining high quality large area h-BN is a significant hurdle in the process of understanding and optimizing scalable graphene growth on such a substrate. A couple of studies have indicated the possibility of obtaining continuous films of graphene on CVD grown h-BN [10,11], but a clear path in this direction has not been tracked yet. Most literature reports nucleation studies of graphene on mechanically exfoliated h-BN flakes [2–5,8,9,12]. Among these, a number of works point towards the formation of round-shaped graphene islands, also referred to as circular pads [3,5], whose crystallinity has not yet been clearly assessed. Other studies report growth of single-crystal graphene grains with a clear six-fold symmetry [2–5,9]. Indeed, at present, it is still unclear which factors influence the development of a proper epitaxial growth and a precise control of the grain shape is lacking. Notably, the only works

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reporting to date a true van der Waals epitaxy with appreciable growth rates are rather complex as they require either a PE-CVD [8] approach or growth catalysts [2]. Furthermore, it is assumed that growth rates of graphene on h-BN are limited to less than 5 nm/min unless growth catalysts are used [2].

In this work we thoroughly investigate the crystallinity of differently-shaped graphene pads and define a clear path for obtaining single-crystal graphene by using a catalyst-free CVD approach. We demonstrate that circular grains display a polycrystalline nature: sectors whose borders can be easily detected via atomic force microscopy (AFM) phase-imaging contain differently oriented graphene patches, as confirmed via Raman spectroscopy. A true van der Waals epitaxy with aligned hexagonal grains can be achieved by simply increasing the hydrogen (H_2) to methane (CH_4) ratio. Indeed, hydrogen acts as an etching reagent, thus reducing the density of nucleation centres. Notably, a fine tuning of the process parameters allows one to achieve growth rates above 100 nm/min.

2. Experimental

We selected single crystal h-BN flakes as the perfect playground for graphene growth investigations. Indeed, the often nanocrystalline nature of the h-BN films grown via CVD greatly hinders the growth of high quality graphene, the partial etching of the insulating crystal being the major hurdle (See [Supplementary information](#)). Flakes of h-BN (from 2D Semiconductors and HQ Graphene) were mechanically exfoliated onto hydrogen-etched silicon carbide (SiC) substrate [14]. SiC was chosen, instead of the classically adopted SiO_2/Si , for its high temperature stability. The low Si sublimation rates of SiC at the adopted growth temperatures avoid formation of carbidic species on h-BN flakes during graphene growth. Typical thicknesses and lateral dimensions of exfoliated flakes ranged between 5 and 90 nm and 10 and 70 μm , respectively

(Fig. 1(a)). The samples were cleaned using a classical approach: first with organic solvents (acetone and isopropyl alcohol) and then loaded inside a resistively heated cold wall reactor used for growth (*Aixtron HT-BM*), and annealed in argon/hydrogen (Ar/H_2) atmosphere (67% Ar , 33% H_2) at growth temperature and 40 mbar for 10 min. Growth was carried out adding CH_4 for 30 min. H_2 to CH_4 ratios were varied from 1:1 to 30:1 to controllably vary the grain shape and crystallinity. Ratios were varied by increasing H_2 flow while keeping CH_4 flow constant. In order to achieve the best growth conditions, growth pressure and temperature were varied between 5 mbar and 150 mbar and between 1000 $^{\circ}C$ and 1150 $^{\circ}C$, respectively.

Raman spectroscopy was used for the analysis of the samples before and after the growth of graphene on h-BN using a Renishaw inVia system equipped with a 532 nm green laser and a 100 \times objective lens. The laser spot size was $\sim 1 \mu m$ and the accumulation time was 2 s. Atomic force microscopy (AFM) was used for surface and height analysis utilizing an *Anasys instruments afm* + microscope operated in tapping mode. The WSxM software package was used to analyse the AFM images [15]. The shape and size of graphene pads was assessed using scanning electron microscopy (SEM) imaging, performed at 5 keV using a *Zeiss Merlin* microscope, equipped with field emission gun. Top-view transmission electron microscopy (TEM) was performed on a *Zeiss Libra 120* operating at 120 kV and equipped with an in-column omega filter for energy-filtered imaging and electron energy loss spectroscopy (EELS) analysis. For TEM analysis, flakes of h-BN were transferred to 1000 mesh copper (Cu) TEM grids (transfer process described in [Supplementary information](#)). X-ray photoelectron spectroscopy (XPS) was performed on flakes transferred to silicon (Si) substrates by using a *Quantera II* from Physical Electronics (PHI). Surveys and core level spectra were collected using an electronically deflected 7 μm X-ray beam focused on the flake of interest with a power of approximately 1.25 W.

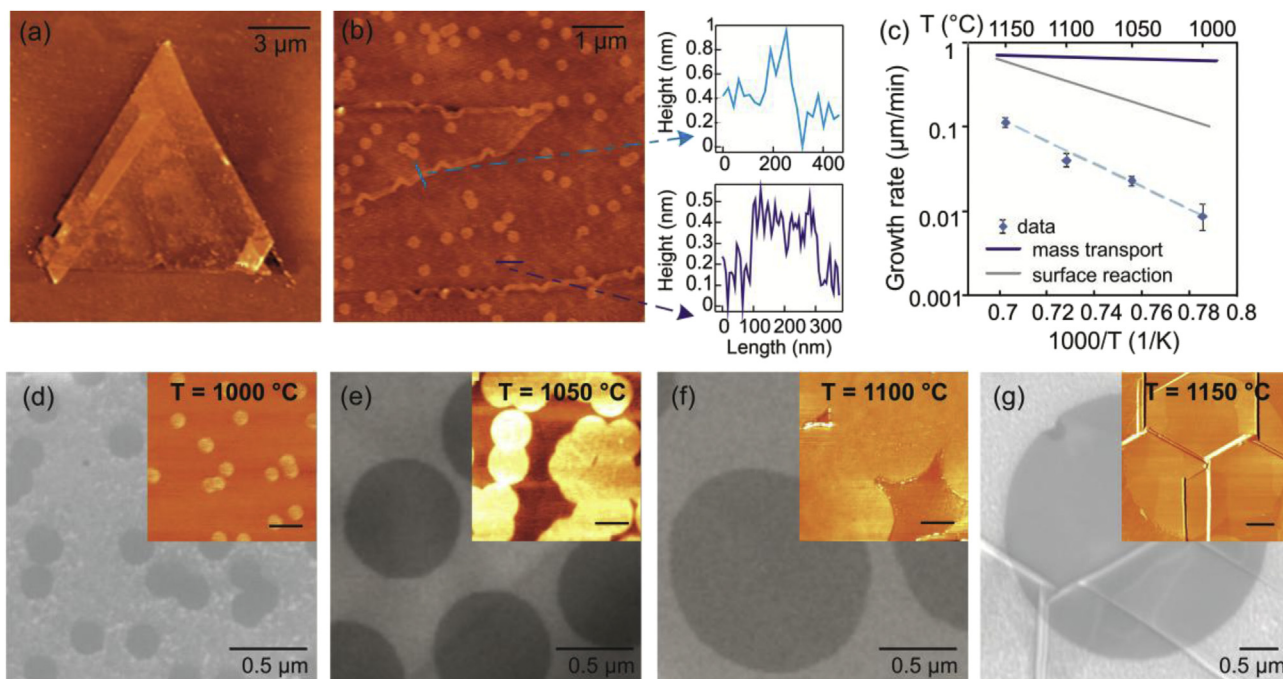


Fig. 1. AFM topography of an-exfoliated h-BN flake before (a) and after (b) CVD growth of graphene. Insets of (b): line profile analysis of the graphene pads (bottom inset) and nanoribbons (top inset) revealing single layer height. (c) Arrhenius plot of the growth rate versus temperature obtained experimentally (diamond markers), calculated for a mass-transport (dark blue line) and surface-reaction limited regime (light grey line). (d–g) SEM micrograph of pads obtained for increasing growth temperatures and corresponding AFM micrographs in the insets (scale bars: 0.5 μm). (A colour version of this figure can be viewed online.)

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