The Adsorption of Hexacontane on Hexagonal Boron Nitride

Juan D. Albar, Vladimir V. Korolkov, Matteo Baldoni, Kenji Watanabe, Takashi Taniguchi, Elena Besley, and Peter H. Beton

*J. Phys. Chem. C, Just Accepted Manuscript* • DOI: 10.1021/acs.jpcc.8b10167 • Publication Date (Web): 13 Nov 2018

Downloaded from http://pubs.acs.org on November 19, 2018

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.
The Adsorption of Hexacontane on Hexagonal Boron Nitride

Juan D. Albar¹, Vladimir V. Korolkov¹, Matteo Baldoni², Matteo Baldoni²,³, Kenji Watanabe⁴, Takashi Taniguchi⁴, Elena Besley² and Peter H. Beton*¹

¹School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD, UK
²School of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK
³Istituto per lo Studio dei Materiali Nanostrutturati (ISMN), Consiglio Nazionale delle Ricerche (CNR), Via P. Gobetti 101, 40129 Bologna, Italy
⁴National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

Abstract

We have investigated the adsorption of hexacontane \((\text{C}_{60}\text{H}_{122})\) on hexagonal boron nitride (hBN) using atomic force microscopy (AFM). The molecules can be deposited either by sublimation or from solution and form lamellar rows with dimensions of the order of 0.1 - 1 µm in three different rotational domains. High-resolution AFM images reveal that, similar to alkanes on graphite, the molecules are adsorbed parallel to the lattice vectors of hBN and we show using molecular mechanics that this corresponds to the lowest energy configuration. Lamellar rows with the same periodicity are observed even when several layers of hexacontane are deposited, although there is some orientational disorder in these multilayers. We also observe heat-induced modification of hexacontane including re-crystallization. We compare our results with recent X-ray studies of alkane adsorption on hBN and discuss the possible role of alkanes on steering molecular self-assembly on hBN.

*peter.beton@nottingham.ac.uk
Introduction

Over the past few decades there has been a continuing interest in the adsorption of alkanes on surfaces, since they play important roles in catalysis\(^1,2\), lubrication\(^3\) and passivation\(^4\). The adsorption of these readily available, low-cost, and non-toxic materials on various surfaces has been studied in depth, particularly on metals\(^5-7\) and graphite\(^8-15\), where they provide a route to promote complex organisation through two-dimensional supramolecular assembly\(^16-20\). In parallel, the recent surge of activities in two-dimensional materials\(^21\) has led to renewed interest in hexagonal boron nitride (hBN), a structural isomorph of graphite. This layered material can serve as an atomically flat tunnelling barrier\(^22\), is mostly free of charge impurities\(^23\) and, when used as a substrate for graphene, greatly improves electrical performance\(^24\). It has also been shown that hBN, both in the form of monolayers grown on metals\(^25-28\) and thicker exfoliated flakes\(^29\), can support the formation of two-dimensional supramolecular assemblies. Furthermore, hBN has been used successfully as a dielectric in organic transistors\(^30,31\). However, the adsorption of alkanes on hBN has so far been studied only using diffraction techniques\(^32,33\) with no direct determination of their real-space arrangement and potential to control supramolecular organisation.

In this paper, we address this question through an investigation of the adsorption of a long chain alkane, hexacontane (C\(_{60}\)H\(_{122}\)), on hBN. The alkane can be deposited either by sublimation or from solution. We find, using atomic force microscopy (AFM), that the alkanes lie flat on the surface with the molecular axis parallel the zig-zag direction of hBN, forming lamellar rows, similar to those formed by long-chain alkanes deposited on graphite. Upon deposition of more than one layer of hexacontane, higher layers are formed which propagate the row geometry, but these are more disordered and weakly bound and are thus more susceptible to heat- and tip-induced modifications.

Experimental

Hexacontane was purchased from Sigma-Aldrich (≥99.8%) and used without further purification. Following our previous work\(^29,34,35\), flakes of hBN with typical lateral dimensions of ~20-50 \(\mu\)m and
thicknesses 10 – 100 nm were exfoliated from high-temperature, high-pressure grown bulk hBN crystals\textsuperscript{36}, transferred onto 5 × 5 mm\textsuperscript{2} of Si/SiO\textsubscript{2} wafers and then cleaned by immersion in toluene (99.9\% CHROMASOLV for HPLC, Sigma Aldrich) overnight followed by heating at 400 °C for eight hours in a flow of 0.15 sl/min of Ar/H\textsubscript{2} (95:5). In addition, samples were flame-annealed immediately before hexacontane deposition. Hexacontane was chosen since it can be deposited either from solution or by sublimation from a crucible in a Knudsen cell resistively heated to 200 °C (this temperature is significantly higher than for many smaller available alkanes, thus minimising the possibility of long term contamination of the vacuum chamber). The pressure during sublimation was 10\textsuperscript{-7} Torr. No heating was applied to the sample during the deposition process. The layer thickness was determined using a quartz crystal thickness monitor which was calibrated from the surface coverage of the dendritic structures formed by hexacontane on the SiO\textsubscript{2} surface\textsuperscript{37}. In the case of solution deposition, the sample was immersed for 1 minute in a solution of hexacontane in toluene (10 µg/ml) under standard conditions. AFM images were acquired using an Asylum Research Cypher-S instrument under standard conditions in conjunction with Multi75Ai-G cantilevers (Budget Sensors). All images were obtained in AC (tapping) mode unless stated otherwise.

Results and Discussion

An AFM image of the surface of an hBN flake acquired after the deposition, by sublimation, of 1 monolayer (ML) of hexacontane is shown in Figure 1. As revealed by a higher magnification image on Fig. 1b, we observe a series of rows running across the surface, and a height profile (inset) along a line perpendicular to them shows that their amplitude is 20 pm and their separation (determined from a Fourier transform) is 7.9 ± 0.2nm. Additional irregular contrast variations are observed due to the roughness of the underlying SiO\textsubscript{2} substrate on which the hBN flake is mounted. These background fluctuations have a peak-to-peak height variation of 50 pm, and a characteristic length scale of ~100 nm, and are not associated with the molecules.
The lines are very similar to those observed when alkanes adsorb on graphite and form lamellar rows in which the linear molecules are stacked perpendicular to the row axis. A higher magnification AFM image on Fig. 1b, shows that the rows on hBN correspond to similar lamellae, in which the individual molecules can be resolved and, as expected, are perpendicular to the row direction. The distance between molecules in the same row is 0.44 ± 0.02 nm, very close to the value reported for alkanes on graphite. The inset shows a profile taken across 20 molecules as indicated by the path in blue. We typically observe domains with area 1 – 5 µm² in one of three orientations with an angular separation of 120° (see below).
To determine the orientation of the molecules with respect to the underlying hBN substrate we employ a protocol which we have previously used in the study of supramolecular heterostructures and the properties of adsorbed molecules on black phosphorus\textsuperscript{38}. By increasing the setpoint used in AFM imaging it is possible to partially remove the alkane chains allowing the local imaging of the underlying substrate. Figure 1c shows an overlay in which the top segment corresponds to the upper half of an image acquired at low setpoint, while the bottom segment is the lower half of an image of the same area acquired at higher setpoint (the complete images acquired at high and low setpoint are included in Supporting Information, SI). The hBN surface shown in Fig. 1c has a coverage of 1ML and the molecular chains can be identified in the upper half of the composite running from bottom-left to top-right. The bottom half of Fig. 1c shows the exposed hBN lattice which allows the identification of the orientation of the lattice vectors. A comparison between the images shows that the molecules run parallel to the lattice vector (the zig-zag direction) of hBN as shown schematically in the structural diagram in Fig. 1d.

The arrangement in Fig. 1d is consistent with a model derived from X-ray studies of alkanes deposited on hBN by Arnold et al\textsuperscript{32} who find two large scale morphologies, including a row-like phase for long-chain alkanes which is in agreement with our results. Although the precise registry of the molecules with the lattice cannot be determined from our images, the results in Fig. 1 are consistent with the placement of CH\textsubscript{2} groups on top of the hexagon centres within the hBN lattice, similar to the widely accepted model proposed by Groszek for linear alkanes on graphite\textsuperscript{39}. The spacing of neighbouring molecules is consistent with that calculated\textsuperscript{9} for alkanes on graphite lying with their carbon backbone parallel\textsuperscript{14}, rather than perpendicular\textsuperscript{13} to the surface. The topographic detail in Fig. 1c is also consistent with this conformation; we see a bright topographic feature in the position attributed to each carbon atom, rather than alternate atoms which would be expected for the perpendicular configuration.
We have investigated the energetics of alkane adsorption on hBN using molecular mechanics employing the LAMMPS simulation package in combination with the Optimized Potential for Liquid Solutions, OPLS potential, which was optimised for long chain hydrocarbons. The hBN substrate was treated as a rigid monolayer with atoms fixed at their crystallographic positions. The Lennard-Jones parameters were taken from Lee. More details are provided in SI. In particular, we have calculated the dependence of the adsorption energy of a single alkane chain on the relative orientation of the molecular axis and the hBN lattice. This has been evaluated through a lateral slide analysis of the potential energy surface (PES) for different orientations of the adsorbed molecule (see Figure 2). A single hexacontane molecule was initially optimized in vacuum; the calculated C-C-C spacing along the chain is 0.255 nm, close to the value taken for the lattice constant of hBN, 0.250 nm. The optimised

Figure 2  (a) Optimised structure of a hexacontane molecule on hBN surface; (b) Adsorption energy as a function of the angle between the principal axis of the hexacontane molecule and the zigzag direction of the hBN lattice; (c) Potential energy surface at 0° rotation and (d) 20°.
hexacontane molecule was then placed at a height 0.35 nm above the model hBN surface, with the plane of the carbon atoms parallel to the substrate. The molecule was next moved as a rigid body along the x and y axes (defined in Fig. 2a) in steps of 0.01 nm as in our previous work\textsuperscript{35}. At each step, the adsorption energy was calculated as $E(C_{60}H_{122}@hBN) - E(C_{60}H_{122}) - E(hBN)$.

Our calculations show that, in agreement with experiment, the lowest energy corresponds to orientations where a hexacontane molecule is aligned with the hBN zigzag direction (as shown in Fig. 2a); the adsorption energy in this configuration is favoured by approximately 0.07 eV/molecule (Fig. 2b). The energies in Fig. 2b correspond to the minimum energies extracted from the PES profiles for each angle of rotation. Examples of the PES profile for alignment angles of 0° and 20° are shown in Figs. 2c,d. After the full relaxation of $C_{60}H_{122}$ molecule on hBN, the adsorption energy at 0° is -5.93 eV (the actual structure is shown in Fig. 2a). The results have also been confirmed for multiple (eight) alkane chains adsorbed on the hBN surface; after the minimisation of the total energy all eight molecules are positioned in the same preferential adsorption sites as in the case of a single chain giving an intermolecular distance of 0.435 nm corresponding to a commensurate arrangement on the hBN layer. The interaction energy between the chains have been estimated as -0.13 eV per each pair. The spacing and orientation of the alkanes are in excellent agreement with our experimental observations.

Figure 3 shows images of hBN on which layers of hexacontane with different thicknesses have been sublimed. For sub-monolayer coverages (Figs. 3a,b) isolated islands are formed with typical lateral sizes of ~1 μm and a height which is comparable to the roughness of the hBN flake. The island at the centre of Fig. 3a is shown at higher magnification (area highlighted in Fig. 3a) in Fig. 3b and from the accompanying height profile (along the red line) we determine a height of 0.4 ± 0.1 nm consistent with a partial monolayer of flat lying molecules. The direction of the lamellar rows is identified by the arrow; the rows run in a common direction for a given island indicating a single extended domain of molecular ordering. An even higher magnification image (area highlighted in Fig. 3b) is shown in Fig. 3c where
the lamellar rows are resolved. The isolated hexacontane islands are rather unstable and after acquiring several images, their shape can be modified, or they can be removed completely; this tip-molecule interaction also accounts for the distortion in the lamellar rows which is prevalent during small scale scans, especially at sub-monolayer coverages.

At a coverage of 2.5ML topographically flat regions co-exist with elongated features with higher apparent brightness (Fig. 3d,e,f); see features highlighted by dashed blue ellipses in Fig. 3d. These features are unstable under scanning, and it is difficult to acquire higher resolution images to reveal additional details of the structure. However, higher resolution images of the topographically flat areas

![AFM images for different thicknesses of hexacontane.](image)
can be acquired which reveal the lamellar rows on the surface; from the coverage, we infer a thickness of 2-3 ML in these regions. A comparison of such images with larger area images indicates that the topographically bright regions in, for example, Fig. 3d, form at, or close to, the boundaries between neighbouring domains with different orientation. Higher resolution images (see Fig. 3f) show that the lamellar rows can deviate from the preferred alignment and show discontinuities and even terminate abruptly in these boundary regions.

As the coverage is further increased to 6.5 ML (Figs. 3g,h,i) an additional superstructure appears in the form of topographically bright features which run perpendicular to the lamellar rows (in this set of figures the orientation of the lamellar rows is determined from the high resolution image in Fig. 3i, which is a zoom of the highlighted region in Fig. 3g). Between these bright regions we observe ‘trenches’ which are topographically dark and also run approximately perpendicular to the lamellar rows (marked by arrows in Fig. 3h). This implies that the lamellar rows terminate at positions which are spatially correlated. We speculate that this may be due to strain relief in the growing film, for example due to a mismatch between the equilibrium alkane spacing and the lattice constant of the hBN.

The lamellar rows and trenches propagate through the growing layer. After the deposition of 10ML these features may still be resolved although the height profile shows that the surface becomes significantly roughened (Figs. 3j,k,l; arrows mark the position of trenches). We do not see further significant changes for thicker layers (Figs. 3m,n,o show images acquired after the deposition of 30 ML). Interestingly, the period of the lamellae is preserved for all coverages studied implying that the substrate directs growth even for these very thick layers.

We have also investigated the effect of post-deposition annealing on the sample morphology (see Figure 4). Figure 4a shows an area on a sample with a coverage of 6.5ML. The high contrast region in the centre of the image is due to a ~4nm thick hBN terrace, and its structure is independent from the hexacontane deposition. Several different orientational domains are observed, and the boundaries
and local orientation of rows are indicated by the turquoise lines and arrows respectively. Figure 4b shows the same area after the sample was annealed on a hot plate at 80°C for 5 minutes (under ambient conditions). A series of faceted rectangular islands with heights in the range 6-8 nm are formed which are aligned with the orientation of rows prior to annealing. The lamellar rows are still present in the regions of the surface between the islands. The formation of islands is attributed to the agglomeration of hexacontane molecules which are depleted from neighbouring multilayer areas in a ripening-type process which leaves a residual monolayer adsorbed on the hBN surface. Figure 4c shows an AFM phase image of an island (area marked with a white box on Fig.4b; the corresponding topography image is included in SI. The lamellar rows are present both on the monolayer-terminated regions between islands and also on the top surface of the islands. Although there is some disorder present, for example in the fluctuating orientation of the rows, the long axis of the island is approximately parallel to the row direction. Interestingly these images suggest that in these hexacontane crystallites the molecules lie parallel to the substrate and the macroscale arrangement
consists of stacks of parallel lamellar rows. Furthermore, the orientation of the interfacial hexacontane molecules directly adsorbed on the hBN appears to propagate through the crystallite, to a first approximation, implying an epitaxial relationship.

Finally, we compare the sublimed hexacontane films with those deposited from solution. A sample is immersed in a hexacontane solution (10 µg hexacontane/mL toluene) for one minute then dried in a nitrogen stream. The molecules form three rotational domains of lamellar structures with an almost identical period 8.0 ± 0.2 nm, misaligned by 120°, as shown in Figure 5. The morphology of these films, which have a thickness of 1 ML, is very similar to the sublimed films but the size of the domains in this case is much smaller, of the order of 100 nm.

Conclusions

Lamellar rows of alkanes are formed on hBN with an internal structure very similar to those observed on a graphite substrate, as confirmed by AFM and molecular mechanics simulations, and in agreement with previous diffraction studies. At higher coverage, the period of the lamellar rows persists and is readily resolved on the surface of multilayers, and, although some disorder is also evident, for example in the form of meandering lamellar rows, this implies that growth is directed by the substrate. The
hexacontane monolayer provides a very simple example of two-dimensional supramolecular organisation. Our results therefore strongly suggest that chain-chain interactions can direct the formation of self-assembled molecular arrays on hBN in an analogous manner to the highly successful approach to supramolecular organisation of complex structures on graphite\[20,17–19\]. In particular, the possible use of hBN raises the possibility of exploring optical properties of such structures which are difficult to access on conducting surfaces, and we believe that this combination of an insulating substrate and van der Waals mediated molecular organisation represents a promising route for the future investigation of the science and technology of surface-stabilised supramolecular arrays.

**Supporting Information Available**

Details of numerical procedures; additional AFM images; examples of AFM-induced modification.

This material can be found online free of charge at http://pubs.acs.org. The original data files including raw AFM images may be found at http://dx.doi.org/10.17639/nott.376.

**Acknowledgments**

This work was supported by the Engineering and Physical Sciences Research Council [grant numbers EP/N033906/1 and EP/P019080/1]; the Leverhulme Trust [grant number RPG-2016-104]. K.W. and T.T. acknowledge support from the Elemental Strategy Initiative conducted by the MEXT, Japan and the CREST (JPMJCR15F3), JST.
References


Table of Contents Figure