Topical Review

Adsorption and epitaxial growth of small organic semiconductors on hexagonal boron nitride

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Abstract
Among ultrathin layered van der Waals materials hexagonal boron nitride has attracted considerable attention. The van der Waals character of its surface together with its insulating properties makes it an ideal substrate for the fabrication of high quality organic crystalline thin films with minimum disturbance from the substrate. hBN can either be used as interface layer decoupling the adsorbed species from the metallic or dielectric support or multilayer hBN can directly serve as an inert, weakly interacting substrate. The adsorbed species and resulting thin organic crystallites can then be considered as almost free standing enabling access to their intrinsic properties. Technologically, this means that organic thin film transistors—ultimately only limited by the intrinsic properties of the organic crystals—can be realized.

The efficient decoupling of the adsorbed organic molecules from the support also provides the opportunity to gain new insights in fundamental aspects of intermolecular interactions, self-assembly, chemical reactions, or electronic properties which might otherwise be inaccessible due to the strong adsorbate-substrate interactions.

In this review, we provide an overview on the adsorption, assembly, growth and properties of organic molecular films from sub monolayer coverages to crystalline thin films on hBN substrates mainly obtained by mechanical exfoliation.

Keywords: hexagonal boron nitride, organic molecules, epitaxy, self assembly, organic electronics

(Some figures may appear in colour only in the online journal)
dependent electronic properties. Thus, crystal quality as well as molecular orientation with respect to the substrate (electrode or dielectric) are crucial. In order to control organic thin film structure, morphology, and quality, a plethora of organic semiconductor-substrate systems has been investigated. High-quality organic thin films have been realized on metallic substrates [6–8], oxide surfaces [9, 10], as well as on layered materials [11–14].

The potential to use small organic or metal-organic molecules as building blocks for self-assembled functional two-dimensional (2D) nanostructures represents also a driving force for intense research [15–17]. Ordered immobilization of individual molecules and their assembly into complex networks might be a pathway towards molecular electronics, selective catalysis, or advanced data storage [18–24].

Especially, the combination of organics with ultrathin, quasi two-dimensional (2D) layered materials like graphene (Gr), hexagonal boron nitride (hBN), or transition metal dichalcogenides (TMDC) is of special interest for the development of improved organic devices [24, 25]. These materials provide atomically smooth and chemically inert surfaces without dangling bonds, perfectly suitable as weakly interacting van der Waals (vdW) substrates for high quality organic thin film growth. vdW-epitaxy [26] allows epitaxial growth of high quality films even for large lattice mismatch between substrate and film. Thus, large organic crystal domains can be grown which are free of structural distortion and charge traps at the interface. The high degree of crystallinity and the large domain size within such vdW heterostructures are desirable for organic field effect applications, since it can be expected that charge carrier mobilities reach values close to the intrinsic limit of the organic material and that the device is free of gate sweep hysteresis [3, 14, 27].

Further, the individual atomically thin layers of these materials are characterized by covalent intralayer bonding imparting significant mechanical strength and stretchability making them extremely robust supports for mechanically flexible organic devices. In addition, the surface strain of a flexural bent material reduces with the substrate’s thickness. Using ultrathin substrates will therefore also enable device flexing which would be impossible for thick bulk material. Besides mechanical flexibility, keeping device structures thin has also other conceptual advantages. For example, 2D material substrates are optically transparent, which is a demand for OLED or light sensor applications. To date, the most important vdW substrates for organic hybrid device design are Gr and hBN. The semimetallic Gr is used as ultrathin, highly conductive, transparent electrode whereas the insulating hBN serves as dielectric. Gr, the prototype of 2D vdW materials, has already been extensively investigated as substrate for organic thin film growth which is well documented in a number of articles and reviews [28–32]. Here, we will put our focus on exfoliated hBN as vdW substrate for highly ordered thin crystalline films and review work done on this topic. We will also have a brief glance on work on molecular adsorption and 2D network formation on hBN to provide some idea about possible processes at the interface at low coverages. First, basic properties of hBN will be presented, followed by a brief section introducing a selection of organic molecules that have been deposited on hBN. Then the most commonly used experimental techniques will be summarized. A section about single molecular layers, multilayers and 2D networks on exfoliated hBN substrates including also CVD grown transferred hBN will be the core part of this review. For the sake of comparison, also a few examples of molecular adsorption and ordering on metal supported hBN nanomesh substrates is attached. Finally, the work is summarized and concluded.

**Hexagonal boron nitride**

2D hBN [33–36] is an insulating isomorph of Gr where covalently bond nitrogen (N) and boron (B) atoms occupy non-equivalent positions. A schematic representation of hBN is presented in figure 1(a). The hBN bulk is formed by vdW stacking of the covalently bond, atomically smooth hBN sheets, whereby nitrogen is positioned on top of boron and vice versa. The in-plane B–N bonding distance is ~0.144 nm whereas the interlayer spacing is ~0.333 nm [37]. The in-plane hBN lattice unit cell parameter $a_{\text{hBN}} = 0.250$ nm is slightly larger than that of Gr $a_{\text{Gr}} = 0.246$ nm resulting in a lattice mismatch of ~1.7% between Gr and hBN [35, 38]. Due to its wide, direct band gap of 5.9 eV [37] it is an optically transparent insulator that absorbs light only in the deep ultraviolet region (>99% transmission in a wavelength range between 250 nm and 900 nm) [39]. With a dielectric constant of $\varepsilon \approx 3–4$ and an electric breakdown field of $E_{\text{break}} \sim 0.8$ V nm$^{-1}$ [40, 41], hBN is well comparable to other dielectrics like SiO$_2$ ($E_{\text{break}} \sim 1$ V nm$^{-1}$, $\varepsilon \approx 3.5–4.5$) [42, 43]. It is also the dielectric of choice for devices purely constructed from 2D vdW materials since it perfectly matches requirements like atomically smoothness, weak interaction, sufficiently high breakdown field, etc [44], and in addition provides high thermal in-plane conductivity compared to other dielectrics ($\lambda_{\text{hBN}} \sim 250–360$ W m$^{-1}$ K$^{-1}$ [45]). Thus, hBN is highly suitable as dielectric for organic (opto-) electronic devices since it is an atomically smooth vdW substrate non-interfering with the organic thin film. Further, it is mechanically flexible and possesses excellent dielectric properties providing a high degree of electrostatic control [44, 46]. In addition, it is optically transparent which is highly desired for opto-electronic applications.

However, basically two types of hBN substrates should be distinguished: hBN mechanically exfoliated from bulk crystals and transferred to some support [12, 33, 35] and epitaxial hBN grown by chemical vapor deposition (CVD) [47–50]. The exfoliated hBN usually exists in few to several 10 μm large flakes with significant thickness variation (see figures 1(c)–(f)). Thus, exfoliation typically yields hBN flakes with thicknesses ranging from single layer to hundreds of layers. Still, exfoliated hBN is atomically smooth, exhibits minimal wrinkling, and is sufficiently decoupled from the substrate. In contrast, larger single-layer hBN domains can be obtained by CVD on transition metal substrates [51]. However, in this case, depending on the substrate, the epitaxial hBN can interact more or less strongly with the metal support influencing hBN’s properties. For example, hBN on...
Rh(1 1 1) is a strongly interacting system resulting in a periodic deformation of the hBN which is often referred to as hBN nanomesh providing ‘pores’ and ‘wires’ (see figure 1(b)) [24, 52–54]. These nanomesh substrates are used as templates to study molecular adsorption and 2D self-assembly [24, 50, 55]. The resulting corrugation of the hBN nanomesh varies with the supporting metal. In case the metal-hBN distance is comparable with the hBN interlayer distance, the corrugation is small, like on Pt(1 1 1) [56], or Cu(1 1 1) [57]. However, irrespective of the metal support, even for small geometric corrugation, a pronounced corrugation of the local workfunction is observed [51] that influences molecular adsorption. Epitaxial, CVD grown hBN can be separated from its metal support and be transferred to other surfaces like SiO₂ by similar procedures as applied to Gr [58, 59]. This opens a way for scalable hBN templates [49].

Small organic molecules

Modern organic chemistry can provide an enormous number of organic components including small molecules, polymers, and highly complex macromolecules. As a consequence of so many degrees of freedom, also the organic materials’ properties vary significantly. The resulting molecular films might be conducting, semiconducting, or insulating, transparent or opaque, soft or hard, chemically inert or highly reactive, etc. However, for the use in organic electronics—and to exhibit decent performance—they have to fulfill certain requirements. For example, they should be processible via standard techniques like vapor deposition or wet processing, be thermally stable, and be stable under operation in electric fields, etc. A subset of the available organic components—that has been successfully used for organic electronics—are small organic molecules [60–63]. They are able to form ordered crystalline structures on a variety of substrates [64] and especially on ultra-thin vdW materials like hBN [65]. On hBN substrates, a number of different small organic molecules has been deposited in order to study adsorption and 2D self-assembly [12, 24, 52, 54, 55, 57, 66], electronic/magnetic and optical properties [67–74], as well as chemical reactions [50, 75–78]. For this review, we have restricted ourselves to a selection of molecules as introduced in the following. A larger collection of molecules exclusively investigated on metal supported hBN can be found in a specialized review elsewhere [50]. In figure 2, the molecular structures of the organic molecules discussed here are compiled. Their general shapes can
be classified as 3D, rod-like (linear), platelet-like (planar), or spherical (0D). While rod-like and platelet-like molecules exhibit high anisotropy in their (electrical) properties, spheri-
cal molecules can be considered to behave isotropically. Large, relatively simple, linear molecules are hexacontane and the slightly kinked diacetylene compound 10,12-nonacosadi-
ynoic acid. Further, shorter but still linear molecules are the rod-like molecules, pentacene (5A), para-hexaphenyl (6P), dihydrotetraazaheptacene (DHTA7) and dioctylbenzothieno-
benzothiophene (C8-BTBT). Whereas 5A and 6P are strictly linear, C8-BTBT is slightly kinked. 2D flat molecules are per-
ylene tetracarboxylic di-imide (PTCDI), as well as naphtha-
locyanine (Nc), tetrap-aminophenyl)porphyrine (TAPP), and tetraakis(4-carboxyphenyl)porphyrine (TCPP). The molecules
melamine, cyanuric acid (CA), trimesic acid (TA), and tere-
phthalaldehyde (TPA) are flat, 2D-like but very small since they are basically consist of only one phenyl ring with small
different side groups. The well-known C60 fullerene is spheri-
cal (0D). Due to its out of plane phenyl groups, rubrene has to be considered as 3D, even though it has a linear tetracene
backbone.

Hexacontane (C60H122) is an alkyl chain of 60 carbon atoms connected via single bonds. It crystallizes in the orthorhombic system with a spacing of ~0.49 nm between parallel chains [79, 80]. 10,12-nonacosadiynoic acid (C29H50O2) is also a long molecule with long alkyl chains. It possesses a diacetyl-
ene core along which an on surface polymerization to con-
ductive polydiacetylene chains is possible [81, 82]. These

very long molecules have to be deposited from solution and tend to form self-assembled stripes with the molecular chains
aligned parallel to each other.

5A (C22H40) is a well-known air-stable molecule which is frequently used in OFET applications because of its compara-
brably high mobility values [83–85]. It is also used for funda-
mental growth studies [86, 87]. It is a p-type semiconductor

crystallizing in a herring-bone bulk structure [88, 89]. Another well studied rod-like molecule crystallizing in herring-bone
bulk structure as well is 6P (C36H28) [90]. 6P provides maximum electroluminescence at around ~425 nm, which makes it attrac-
tive for OLED applications [91]. Additional interesting properties like blue lasing have been reported [92]. However, 6P has mainly been used as a representative model molecule to study the growth of small rod-like organic molecules on various substrates [12, 32, 93–97].

A rather recently synthesized linear molecule is DHTA7 (C26H16N4) [98–100]. Its structure is based on heptacene where four CH groups are replaced by N and NH, respectively (see figure 2). The modification breaks the molecule’s symmetry and results in a dipole moment and H-bonding between the molecules which orients neighboring entities in head-to-tail
arrangements. As a result, the bulk structure deviates from the herring-bone configuration enabling increased π–π stacking [99, 100]. Since, the molecules carry a small, but permanent dipole moment film growth might also be influenced [25].

C8-BTBT (C30H40S2) is one of the small organic molecule materials with the highest mobility and can be either solution
processed [101–103] or vapor deposited [104]. C8-BTBT pos-
 sesses a flat core part with alkyl chains on both sides. In the bulk structure, the core parts arrange in a herring-bone fashion with parallel alignment of the alkyl chains [105]. C8-BTBT forms layered films exhibiting p-type conductivity with field effect mobilities up to \( \mu_{\text{FET}} \sim 30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) [104, 106].

An example of planar organic semiconductor molecules is
PTCDI (C24H20N2O2), which can be vapor or solution depos-
ited. It consists of a perylene core to which two imide groups are attached.

The phthalocyanine derivative Nc (C48H26N8) is a prototype of a planar molecule, which is a large aromatic, macrocyclic
organic molecule with extended π-system. Similar in geometry and size are the porphyrine base TCPP (C44H42N4O4) and
TAPP (C44H42N4O4) molecules. They consist of a porphyrine core with either amino phenyl groups (TAPP) or benzoic acid
 groups (TCPP) attached. These large planar molecules can be

used, for example, as building blocks for self-assembled 2D
networks on surfaces [107–109].

Rubrene (C28H28; 5,6,11,12-tetraphenylanthracene) is a red-colored chiral aromatic hydrocarbon consisting of a twisted tetracene backbone flanked by four out-of-plane phenyl groups, which make it non planar. It is known for its record hole mobility of \( \mu \sim 40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) [110], which is only reached for perfect single crystals [111]. Films can be prepared by vapor deposition as well as by solution processing. Rubrene can crystallize in several polymorphs which are monoclinic [112], triclinic [113], and orthorhombic [114, 115]. It has also been frequently used to study molecular organization on noble metal surfaces [116, 117].
The simplest way to prepare C60 thin films is vapor deposition. It is an n-type organic semiconductor which makes it an interesting material for bulk heterojunction solar cells [118, 119]. The C60 buckminsterfullerene is a cage-like spherical molecule with an approximate diameter of 0.7 nm. In the crystalline bulk phase it adopts an fcc structure at room temperature. In the experimental methods. Here, we provide just a brief overview of some of the main preparation and characterization techniques.

Preparation of hBN substrates

So far, there are three main approaches to fabricate hBN substrates. First, there is mechanical exfoliation in a similar way as introduced for Gr by Novoselov and Geim [35, 36, 120]. The second is epitaxial hBN growth by a CVD method on various metal catalyst surfaces [36, 39, 121–126]. The third technique is liquid exfoliation [127] which allows larger scale fabrication of hBN nanosheets. Besides the established main techniques also novel approaches are explored like ion-intercalation assisted exfoliation [128], physical vapor deposition [129], surface segregation-based methods [130], pulsed laser deposition [131], pyrolysis [132], or unwrapping of BN nanotubes [36, 133].

Mechanic exfoliation can be done from larger hBN single crystals [41] or from crystalline powder [35, 134]. The results are usually flakes with strongly varying vertical and lateral dimensions. In vertical dimension, the flakes can be single layer, few layers, or several 100 or 1000 layers thick. The lateral dimensions usually range from a few µm to tens of µm as can be seen in figures 1(c)–(e)). As support for the flakes often SiO2/Si wafers are used with thermal oxide thickness of either 80 nm or 285 nm. These oxide thicknesses are chosen to obtain a sufficiently high optical contrast making even single layered flakes visible by optical microscopy. Even though direct mechanic exfoliation is a comparably fast and simple way to receive thin hBN flakes it needs practice to be routinely applied. A major drawback of the method is the poor control over the flake dimensions, which complicates a targeted substrate preparation. However, the obtained flakes are usually pure and of high crystalline quality with minimal wrinkling.

A way for large-scale fabrication of 2D hBN nanosheets is liquid exfoliation [135, 136]. Within this approach boron nitride powder is sonicated in an appropriate solvent that minimizes the energy of exfoliation. For hBN, a variety of possible solvents facilitating mechnano-chemical exfoliation but also flake’s functionalization has been reported [135–143].

As classical surface science technique, epitaxial growth by CVD is a highly controllable and scalable process, to obtain large-area, single or multilayer hBN. In the process, a gaseous precursor (e.g. borazine (B3H6N3), and ammonia borane (NH3-BH3)) is brought into contact with a catalyst surface which triggers the chemical reaction and acts as epitaxial template. The result is usually a large-area polycrystalline hBN sheet which is in intimate contact with the catalyst and needs to be subsequently separated and transferred to the desired substrate. As catalysts, polycrystalline materials like Cu foils [39], Pt foils [59], or Ni films [121] have been used in flow reactors or furnaces. Well-ordered monolayer hBN films can be generated by CVD on single crystalline substrates like for example Ni(111) [144], Rh(111) [54], Ir(111) [125], Cu(111) [145], or others [36] under UHV conditions. In case a transfer is desired, the CVD grown hBN film is covered by a polymer layer, usually polymethylmethacrylate (PMMA), for protection and handling. The hBN/PMMA assembly is then removed from the catalyst either by etching away of the catalyst or by electrochemical delamination [58, 59]. After that the hBN is brought into intimate contact with the desired substrate—most often SiO2/Si- and the PMMA is removed by dissolving it in acetone.

Organic thin film deposition

Basically, all classical vapor based or solution based deposition processes can be applied to deposit organic molecules on the hBN surface. The main methods applied in the framework of this article are vapor deposition techniques like organic molecular beam epitaxy (OMBE) [146], hot wall epitaxy (HWE) [147], and vapor deposition in tube furnaces with and without carrier gases. OMBE—operated under ultra-high vacuum (UHV) conditions—is suitable to controllably deposit small amounts of molecules, which is necessary for studying very small coverages and for the development of 2D molecular networks.

HWE is a vapor deposition technique operated under high vacuum conditions (∼10⁻⁶ mbar) that potentially allows to grow very close to thermodynamic equilibrium conditions and turned out to provide very good results for crystalline organic thin films [11–13, 148]. The closed bottom of a semi open, vertical quartz tube is filled with the organic material in powder form. The open side of the tube is closed by the substrate. The tube bottom, the substrate, and the tube wall can be heated independently. In this way, the evaporation rate, vapor temperature, and substrate temperature can be adjusted separately for optimal growth conditions.

Closely related to HWE is the vapor deposition technique in furnaces or tube reactors when operated without carrier gas [14, 104]. There, the source material and the substrate are arranged adjacent but at some distance to each other in a horizontal tube. A heating system generates a temperature gradient, where the temperature is highest at the position of the source material and lowest at the tube endings. The organic vapor deposits on the substrate which is at lower temperature than the source. The growth parameters are optimized by controlling the temperature and adjusting the distance between source material and substrate. Often, carrier gases like Ar, N2, H2, or mixtures of these are used that flow from the source region towards the substrate [149–153].

Solution based deposition can happen via immersion, drop casting, spin coating, etc, of solutions which contain organic
molecules [154]. The film properties can be adjusted by the constituent concentration, choice of solvent, immersion time, and temperature. Solution based techniques are insofar interesting since they do not need elaborate vacuum equipment, which saves time and costs.

**Characterization**

For insulating thicker hBN layers on metals supports or dielectric substrates, atomic force microscopy (AFM) [155, 156] methods are often applied. Unlike STM, which does not work on insulators, the AFM relies on a force feedback which also works on insulating surfaces. Most AFM systems operate under ambient conditions and are used to resolve structure sizes from several 10 nm to several 10 µm. Since AFM systems providing molecular resolution are meanwhile commercially available they are frequently used to determine molecular arrangements and surface unit cells. Thus, they play a similar role on insulating surfaces as STM does on conductive systems.

For epitaxial, single-layer hBN still attached to the metal substrate, scanning tunneling microscopy (STM) [157] is a frequently used standard method to characterize molecular assembling on hBN at molecular and atomic resolution [24, 50]. It also allows to perform local manipulations by application of voltage pulses, which can be used to trigger and to investigate local chemical reactions between the molecules on the surface [75, 76, 158].

Due to the limited thickness of the organic films, structural investigations using x-rays are often performed using grazing incidence x-ray diffraction (GIXD) [159, 160]. In GIXD, a collimated x-ray beam is directed at an incidence angle <1° to the sample surface. In order to determine the in-plane structure, the sample is rotated in-plane and the diffracted intensity is recorded as a function of rotation angle. For organic mono or few-layer samples, GIXD is often performed at synchrotron radiation sources to realize sufficient signal intensity [159, 161] but can also be performed with standard laboratory equipment [162]. However, care has to be taken when using highly intense x-ray beams at synchrotrons, since they might cause damage of the relatively sensitive organic films [163].

Angle-dependent near edge x-ray adsorption fine structure spectroscopy (NEXAFS) is a method to determine the local geometry and chemical state of atoms or molecules adsorbed on surfaces [164]. Since for NEXAFS the energy of the incident x-ray has to be tuned to track an energy window around a specific absorption edge, a synchrotron light source is necessary. For organic materials, often the carbon K-edge is investigated (280–300 eV). Intensity changes as a response to a variation of the beam incidence angle can be used to determine the molecular tilt angle with respect to the substrate [165].

Transmission electron microscopy (TEM) is a powerful technique for structure characterization with potential atomic-resolution imaging in real space [166]. In order to enable electron transmission for TEM measurements, specimens have to be thinner than ~100 nm (material dependent). Thin organic layers on hBN flakes are naturally thin samples which only can be transferred to, or prepared directly on the TEM grid without further treatment. In this way, selected area electron diffraction (SEAD) patterns can be recorded, which is useful for the determination of local unit cell parameters and orientations [49]. However, organic films are comparatively sensitive and electron beam damage effects can limit the reliable use of TEM for organic materials [167].

The majority of the techniques mentioned so far mainly aim on structural/geometrical properties. They can be complemented by techniques which are sensitive to chemical changes and (opto) electronic properties. A frequently used standard tool for qualitative and quantitative chemical analysis of surfaces is x-ray photoelectron spectroscopy (XPS) [168] which can be performed with standard lab apparatus or at a synchrotron if very high energy resolution or high sensitivity are necessary. For the measurements UHV is required. X-rays with energies around 1.5 keV for lab sources (for synchrotrons up to 20 keV) generate photoelectrons from core levels which are analyzed by their kinetic energy which is specific for their binding energy. Chemical interaction can cause core level shifts, which are then detected. Sensitive to binding configurations and chemical surrounding is also Raman spectroscopy [169]. Raman spectroscopy relies on inelastic scattering of monochromatic light at molecules or solids. Laser light is focused to the sample and interacts with molecular vibrations. Laser photons can change their energy by either exciting or absorbing phonons which is detected as frequency shift in the scattered light. From the spectrum potentially parameters like crystallinity, crystal orientation, chemical composition, strain, temperature, doping, etc., can be deduced.

Also light absorption spectra recorded in the ultra-violet, visible and near-infrared region (UV–vis-NIR) can be used to gather information about the electronic properties of the organic compounds. The wavelength dependent absorption provides information about important parameters like the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [107]. For example, from the comparison of the HOMO–LUMO gap measured in solution or gas phase with the gap of the adsorbed material conclusions about the binding strength can be drawn [170, 171]. It is also a powerful tool when polarized light is used. Many organic molecules are anisotropic in shape and light absorption. Polarization direction dependent absorption provides information about preferential molecular orientation and can reveal domain structures [172].

**Density functional theory**

In order to properly interpret experimental data, density functional theory (DFT) [173] is widely applied. DFT has been very successfully applied to many solid state problems. DFT is especially powerful for the calculation of equilibrium structures and, for example, has been successfully applied to inorganic thin films on metal surfaces [174, 175]. However, when dealing with organic molecules on surfaces like hBN a special approach is needed to account for vdW interactions,
e.g. by employing the Tkatchenko–Scheffler [176, 177] or the Grimme schemes [178]. Structural models, adsorption geometries, or spatial arrangement of molecular orbitals can be simulated. Different scenarios/structural models can be tested, and the results are then compared with the experimental evidence. DFT is especially useful to identify preferential adsorption geometries of individual molecules by comparing the corresponding binding energies of possible adsorption configurations. This can help to understand the alignment of the evolving molecular structures [12, 14, 104]. Further, analysis of the orbital overlap helps to understand the structural-electrical conductivity relation [14].

Results and discussion

In the following, experimental data supported by theoretical modelling of the growth of organic molecules on different types of hBN substrates is provided. The focus is set on the work done on exfoliated hBN substrates. For the sake of comparison, we only touch the topic of adsorption and ordering on metal supported hBN. Metal supported hBN substrates are a wide topic and not the focus of this work. For a broad and detailed overview on this special topic, the reader may be referred to the recent review by Auwärter [50].

Epitaxial multilayers and crystallite growth on exfoliated hBN flakes

hBN is considered to be a perfect candidate for gate dielectrics in OFETs. On the one hand it nicely isolates the organic channel material from the gate and on the other hand the atomically smooth vdW surface enables a trap-free hBN-organic interface and the growth of high quality organic thin films with a high degree of crystallinity.

Rubrene on exfoliated hBN

An exceptionally high field effect mobility of $\mu \sim 11.5 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ has been achieved for high-quality rubrene films grown on exfoliated hBN [161]. This value lies already within the range of free standing rubrene single crystal FETs ($\mu \sim 15 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) [179] and clearly above those of rubrene thin film FETs with conventional SiO$_2$ gate dielectric ($\mu \sim 8 \times 10^{-6} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ [180]). In this case, vdW-Gr bottom contacts were employed in order to ensure minimum distortion of the film and low contact resistance. The values almost reached those of devices with high quality single crystal rubrene suspended over an air-gap [179], which was attributed to the atomically sharp, low trap density hBN/rubrene interface. As substrates exfoliated hBN flakes transferred on SiO$_2$/Si supports were used. For device fabrication, smooth flakes of uniform height of 10–60 nm and lateral sizes larger than 10 $\mu$m were selected. 500–1000 nm thick rubrene films were grown by a vapor transport method at a substrate temperature of $\sim 450 \text{K}$ and a growth rate between 16 and 33 nm s$^{-1}$ [161]. The resulting rubrene films formed large single crystalline domains essentially limited only by the flake size. A structural model of the rubrene molecular arrangement on hBN is provided in figures 3(a) and (b). AFM revealed the existence of atomically smooth, uniform terraces with a typical step height of $\sim 1.4 \text{nm}$. TEM image and SAED pattern of rubrene on hBN are shown in (d). The red circle in the bright field TEM image on the right side of (d) indicates the position for SAED. In the diffraction pattern on the right side of (d) the rubrene (200) (orange) and (020) (yellow) as well as the hBN $\{10 \ 10\}$ reflexes are indicated. The dotted orange and yellow lines indicate the corresponding rubrene reciprocal planes. (c), (d) [161] John Wiley & Sons. © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
locked to the directions of the 3-fold symmetric hBN crystal. Apparently the weak rubrene/hBN interaction is still sufficiently strong to promote epitaxial ordering of rubrene on hBN, but not strong enough to severely distort the rubrene lattice. GIXD and SAED revealed that the $a$-axes of hBN and the rubrene lattices are rotated by $\sim 3^\circ$ (GIXD) to $\sim 4^\circ$ (SAED) with respect to each other. First-principle binding-energy calculations for a single rubrene layer on hBN as a function of the relative rotation angle between their $a$-axes revealed—consistently with the experimental data—energy minima at rotation angles smaller than $10^\circ$. Calculations including vdW interactions yielded optimum misorientation angles of $\sim 6^\circ$ which corresponds to reduction in energy of 0.2 eV per molecule in comparison to the computations excluding vdW contributions [161]. This further indicates that the weak vdW interaction can be important for epitaxial growth.

**C$_8$-BTBT on exfoliated hBN**

The fact that the vdW forces between molecule and substrate are often significantly weaker than the mutual molecular interaction can be exploited to obtain quasi free standing molecular crystals with minimum interference from the substrate. This way, high-quality few layer thick films of diocetylbenzothieno- endibenzo[1,2-b:2',1'-d]thiophene C$_8$-BTBT exhibiting record charge carrier mobilities have been fabricated on Gr and hBN [104, 106]. In this case, exfoliated hBN substrates transferred onto SiO$_2$/Si supports (285 nm oxide thickness) were used. The C$_8$-BTBT crystals were grown in a tube furnace at $\sim 5.3 \times 10^{-6}$ mbar without carrier gas by heating C$_8$-BTBT powder to 100 °C–120 °C. The substrates were just positioned a few inches away from the source. Unfortunately, the sample temperature is not specified, but should lie below the source temperature and above room temperature. To study the evolution of the film, the growth process was interrupted in order to perform ex-situ AFM measurements at different growth stages. The thickness of the initial three layers were determined to be $\sim 0.53$ nm (interface layer), $\sim 1.68$ nm (first layer) and $\sim 2.85$ nm (second layer) as shown in figures 4(b)–(d). The subsequent higher layers exhibited slightly higher heights around $\sim 3$ nm which corresponds well with the layer distance specified for C$_8$-BTBT bulk ($\sim 2.9$ nm) [101, 105, 181]. The interface layer with a thickness of only $\sim 0.53$ nm indicates a molecular packing different from the bulk. STM studies on the C$_8$-BTBT interface layer on Gr, which behaves very similar as the C$_8$-BTBT/hBN system, suggest molecular packing in a rectangular lattice with $d_1 = 2.52$ nm and $d_2 = 0.66$ nm [104]. Corresponding DFT calculations resulted in an optimized geometry for a single C$_8$-BTBT on Gr where the alkyl chains are almost parallel to the Gr and the molecule exhibits a leaning angle of $\sim 35^\circ$ with respect to the ‘stand-up’ configuration. (In the ‘stand-up’ configuration, the benzothienophene is parallel to the surface whereas the alkyl chains stick out of the Gr plane with a height of $\sim 1$ nm.) In this configuration, the CH-$\pi$ [182] and $\pi-$ $\pi$ [183] interactions are maximized. A fully relaxed structure including molecule–molecule interaction resulted in a tilt angle of the benzothienophene plane with respect to Gr of only $10^\circ$ and a lattice with $d_1 = 2.47$ nm and $d_2 = 0.64$ nm and a layer thickness of $\sim 0.52$ nm which coincided perfectly with the STEM data. A schematic representation of the approximate position of the C$_8$-BTBT molecules of the IL with respect to the hBN is shown in figure 4(a)). Interestingly, the alkyl chains tend to align roughly with the hBN’s zigzag direction. A perfect alignment of the alkyl chain with the zigzag direction was found for the adsorption of hexacontane on hBN [184] (see later). High-resolution AFM images (figures 4(e) and (f)) of the first and second layer growing on top of the interface layer revealed a monolinic crystal structure with herring-bone stacking similar to the bulk configuration. The lattice parameters were found to be $a = 0.67$ nm and $b = 0.79$ nm which is slightly different from the bulk values. Further, the molecules in the first layer appeared to be more inclined as would be expected for the bulk [102]. Apparently, the substrate’s influence is already reduced in the first layer and already negligible for the second layer. That is also reflected in the calculated binding energy of an individual molecule in the first layer on top of the interface layer which is 0.048 eV for the hBN substrate. The corresponding intermolecular binding energy in the first layer is 0.704 eV. That clearly demonstrates again that the influence of the substrate (interface layer) is very small compared to the intermolecular interaction. This fact is also reflected in the morphology where a small nucleation density and large islands with smooth rims were observed indicating high diffusion rates on the substrate and along the island rims. The high crystalline quality obtained on the smooth and only weakly interacting hBN substrate is also evident in the charge carrier mobility, which is very sensitive to structural defects. Mobility measurements were performed on C$_8$-BTBT OFETs with hBN gate dielectric and transferred Au top contacts as a function of film thickness and temperature [104, 106]. Even though the C$_8$-BTBT channel only comprised from the interface layer and the first layer, field effect mobility values of up to $\mu \sim 10$ cm$^2$ V$^{-1}$ s$^{-1}$ were reached [104]. These high values basically correspond to monolayer devices since it can be assumed that the interface layer is non-contributing. The observed field effect mobility outperforms typical values found for monolayer devices by orders of magnitude ($\mu \sim 10^{-6}$–$10^{-7}$ cm$^2$ V$^{-1}$ s$^{-1}$). Measurements of the intrinsic hole mobility utilizing a gated four-point probe technique revealed values up to $\mu \sim 30$ cm$^2$ V$^{-1}$ s$^{-1}$ for first layer devices [106]. After optimization of the contacts by insertion of a doped Gr layer, C$_8$-BTBT OFET devices showed clear band like transport and superior characteristics. Interestingly, devices with a higher number of C$_8$-BTBT layers performed worse, which was attributed to the low charge transport between the layers [106]. However, the high mobility values obtained are a consequence of the high crystal quality and large domain sizes. It could be further shown that C$_8$-BTBT preferentially grows in a layer-by-layer fashion on hBN and that an out-of-plane roughness just larger than 0.6 nm is sufficient to trigger additional nucleation [185]. At coverages beyond two monolayers, the roughness is already significantly larger than 0.6 nm resulting in increased nucleation and smaller domain sizes which could reduce mobility.

However, based on the C$_8$-BTBT/hBN OFET system [104, 106] it could convincingly be demonstrated that these
kinds of single layer devices are advantageous because of the direct contact with the charge transport layer, the conserved intrinsic mobility and the minimized parasitic contact resistance.

**Pentacene on exfoliated hBN**

Exfoliated hBN has also been used as vdW substrate for the growth of high-quality, few layer pentacene (5A) in order to study 5A’s intrinsic electrical properties in the 2D limit \[14, 65\]. For this study, hBN was especially suitable because, first, it is an atomically smooth vdW material with low defect density and, second, it has a comparably low dielectric constant which yields only weak polaronic coupling. The smooth vdW surface is crucial for the growth of high-quality crystals with little disturbance from the interface, thus minimizing disorder, charge trapping, etc. The low polaronic coupling at the organic/hBN interface reduces the possible Fröhlich polaron \[186\] related reduction of the mobility in the film \[187, 188\], which might cause deviations from the intrinsic values.

Sample preparation was performed the same way as explained for C\(_8\)-BTBT. Just the furnace temperature was 130 °C–160 °C in this case. A typical growth time for a 5–10 layer thick 5A crystal was 3h. Analogous to C\(_8\)-BTBT, the procedure resulted in layered crystals as confirmed by AFM and TEM investigations. Here, again an interface layer of only 0.5nm height followed by two layers with heights of 1.14nm (first layer) and 1.58nm (second layer) occurs (see figures 5(a)–(d)). All subsequent layers had the same height as the second layer which corresponded well to the terrace height in the 5A thin film phase \[189\]. The small height of the interface layer implies a flat-lying configuration of 5A with its long molecular axis oriented parallel to the hBN’s zigzag direction (figure 6). A flat-lying configuration of molecules is frequently observed for 5A on a variety of substrates \[190–192\].

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**Figure 4.** C\(_8\)-BTBT on exfoliated hBN. (a) Approximate alignment of the C\(_8\)-BTBT molecules in the interface layer (IL) on hBN. (b) Schematic side-view of the first three molecular layers. The marked layer heights correspond to the average values measured by AFM. (c) AFM image indicating the different C\(_8\)-BTBT layers on hBN, and (d) a corresponding height histogram of the measured layer thickness. (e), (f) molecularly resolved AFM images with assigned unit cell vectors of the first (1L) and second (2L) C\(_8\)-BTBT layer. (e)–(f) \[104\] © 2014 Macmillan Publishers Ltd. All rights reserved.
High-resolution AFM measurements revealed a unit cell of the first layer which is ~3.3% larger along the $a$-axis than that of the second layer. TEM and SAED of 5A/hBN films revealed lattice constants for the second layer ($a = 5.98 \pm 0.09\ \text{Å}$, $b = 7.61 \pm 0.13\ \text{Å}$) (see figures 5(e) and (f)) and angle between the unit cell vectors ($\alpha = 88.3 \pm 1.2^\circ$) that correspond well to the 5A thin film phase. Analysis of the SAED patterns from several different few-layer 5A crystals showed mostly an angle of 16° between the 5A(0 1 0) and the hBN(1 0 0) crystal orientation indicating a quasi-epitaxial relationship between 5A and hBN. The quasi-epitaxy was explained to arise from the weak vdW interaction with the substrate and the incommensurability between 5A and hBN. However, the presence of other angles indicated that the epitaxy is not perfect. DFT calculations of the relaxed first and second layer structures agreed within 1.5% with the experimentally found structures. The 5A packing in each layer is determined by the competition between interlayer and intralayer interactions. The flat

Figure 5. 5A on exfoliated hBN. (a) Schematics of the vertical stacking of the first three 5A layers. The indicated layer thicknesses correspond to the average height measured by AFM. AFM images of steps between (b) IL and 1L, (c) 1L and 2L, and (d) hBN and IL. (e) Histograms of the measured lattice constants of the 5A $a$-$b$ plane for the 1L and 2L (blue and red colors represent the $a$- and $b$-axes, respectively). (f) Schematic of the molecular packing in the 1L (blue upper panel) and the 2L (red lower panel). (b)–(f) Reprinted with permission from [14]. Copyright (2016) by the American Physical Society.
Interestingly, second layer devices showed bandlike charge transport mechanism \[14, 194, 195\]. The difference in transport mechanisms of the first and second layer was rationalized by calculating the molecular orbitals of the intermolecular bonding states. Indeed, continuous overlap was found for the second layer whereas the overlapping orbitals only span five molecules in the first layer reducing the travel length of a charge carrier to only \(\sim 1\) nm. 5A OFETs with three or more layers had similar maximum room temperature mobility as two-layer devices indicating that the interface induced modulation of the molecular packing and transport are insignificant beyond the second layer. The significance of hBN as gate dielectric becomes apparent when comparing the device performance of single layer 5A FETs with classical SiO\(_2\) dielectric. First single and double layer 5A FETs with SiO\(_2\) gate dielectrics were realized by physical vapor deposition with nitrogen as carrier gas \[197\]. Using classical top source-drain electrode contacts fabricated by vapor deposition of 30 nm of gold, mobility values of only \(\mu \sim 0.01\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) were achieved for single layer 5A FETs and \(\mu \sim 0.15\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) for double layer devices. A mobility improvement for a single layer device to \(\mu \sim 0.015\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) was realized by employing bottom gold contacts modified with self-assembled layers of perfluoro octanethiol to optimize contact resistance \[198\]. A tremendous mobility improvement for single layer 5A to \(\mu \sim 0.31\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) was achieved when a polystyrene layer was spin coated on the SiO\(_2\)/Si substrate prior to 5A deposition and when a special soft imprinting method for placing the gold source and drain contacts was applied. Even though significant improvements have been demonstrated, the mobility values are low compared to the 5A FET with hBN dielectric. The reason is that the single layer 5A films on conventional and modified SiO\(_2\) are still polycrystalline with a significant density of grain boundaries that dominate the charge transport and permit hopping transport only.

**Para-hexaphenyl on exfoliated hBN**

Even though the vdW interaction between hBN and organic compounds is weak, it is evidently still sufficient to promote a quasi-epitaxial alignment of the organic crystal with the hBN substrate. This has been also exploited to grow self-assembled para-hexaphenyl (6P) needle networks with discrete needle orientations with respect to the substrate \[12\]. As substrates, hBN exfoliated from powder and subsequently transferred on SiO\(_2\)/Si substrate (80 nm oxide thickness) were employed. Typical lateral hBN flake sizes in the range of 5–30 \(\mu\)m were obtained with varying heights between 0.6 nm to several tens of nm. 6P was deposited via hot-wall epitaxy \[147\] under high vacuum conditions (\(p \sim 2 \times 10^{-6}\) mbar) at substrate temperatures \(T_D\) between 300 K and 400 K at a growth rate of \(\sim 9 \times 10^3\) molecules \(\mu\)m \(^{-2}\) s\(^{-1}\). After a typical growth times of \(\sim 5\) min, the 6P coverage was \(\sim 0.6\) monolayers (one monolayer (ML) refers to the packing density in the 6P (001) plane: \(\sim 4.4 \times 10^{14}\) molecules cm\(^{-2}\) \[199, 200\]). The resulting film morphologies were characterized using intermittent contact mode AFM.
under ambient conditions. The morphology was dominated by needle-like structures as can be seen in the AFM image in figure 7(a). Their average lengths ranged—depending on the growth temperature—from several 100 nm ($T_D = 298\,K$) to several $\mu$m ($T_D = 393\,K$). Occasionally, at $T_D > 380\,K$ individual needles of up to 30 $\mu$m length were found, only limited by the hBN flake’s size. 6P needles have been frequently observed and were identified to be crystallites composed of molecules with their long axes oriented parallel to the substrate surface [64, 201]. Similar to the behavior of 6P on Gr [11, 32, 97, 172], the needles’ long axes on hBN followed six discrete growth directions which grouped in three pairs of two with around $-10^\circ$ in between, and $-60^\circ$ in between the three pairs (see fast Fourier transformation image in figure 7(b)).

DFT calculations revealed that individual 6P molecules adsorb with their long axes parallel to hBN’s armchair direction with the phenyl rings centered on the nitrogen atoms (see figure 6). With increasing coverage, the individual molecules—aligned with the armchair direction—attach along their long molecular axes and form stable nuclei. From there, growth proceeds preferentially in the direction perpendicular to the long molecular axes (in this case, the hBN zigzag direction). However, the evolving structure is 3D, and the vdW molecule-substrate interaction is weak. Thus, intermolecular interactions dominate and drive the molecular system towards its bulk equilibrium structure. For 6P under the applied temperature regime this is the 6P $\beta$-phase herring-bone structure (Baker structure) [90, 96]. In order to minimize the system energy, a contact plane of the 6P bulk is chosen that causes the smallest possible strain between the interfacing molecules in their preferred adsorption sites and the 6P bulk. In this case, the 6P contact plane fulfilling the requirements best was the 6P($-6.29$) plane [96] which was, for example, also found for 6P on Cu(1 1 0) [202]. As shown in figure 7(c), starting from the ($-6.29$) plane with a single 6P in its preferred adsorption geometry on hBN we obtain a needle growth direction which is $-6^\circ$ tilted with respect to the hBN zigzag direction. The mirror symmetry of the system implies a second equivalent growth direction which is rotated by $2 \times 6^\circ = 12^\circ$. Thus, a $\pm 6^\circ$ splitting from the zigzag direction is expected in good agreement with the observations.

Further, with increasing substrate temperature more and more needles followed the discrete growth directions indicating that such an alignment is energetically preferred. A comparison of the 6P growth morphologies between different hBN thicknesses revealed that hBN flakes thinner than three layers did not support growth of long needles [12]. This was attributed on the one hand to surface roughness which was translated from the interface with the SiO$_2$/Si support through the very thin layers and on the other hand to the low dielectric constant of hBN that caused insufficient screening of dipole fields arising from trapped water at the interface. Thus, a flake thickness of at least $\sim 1.5\,nm$ was needed to cancel out interference from the support.

For such ordered 6P needles on hBN, the influence of the vdW interface on the nanoscale friction between organic crystallites and Gr and ultra-thin hBN has been studied by means of AFM manipulation and was compared to 6P needles on Gr [203]. It was shown that crystalline 6P nano-needle fragments preferentially moved along their preferred growth directions rather than directly following the primary pushing direction given by the AFM tip movement. Further, application of a torque by the AFM resulted in rotation of the crystallites. When crossing the preferential sliding/growth directions of the needles a significant increase of the torsional signal of the AFM cantilever was observed. Supported by molecular dynamics simulations, it turned out that the clear frictional anisotropy and preferred sliding directions are determined by the complex epitaxial relation between organic crystallite and 2D substrate. It takes higher forces to reorient the crystal from its original directions because it has to leave its commensurate state. Once the crystal is out of the commensurate state, it can be easily moved until another commensurate state is hit and the crystallite locks again. Even though the interaction between the vdW substrate and the organic molecules is

![Figure 7. 6P on exfoliated hBN (a) AFM image of an hBN flake covered with a 6P nanoneedle network. (b) FFT image of (a) clearly revealing discrete needle growth directions. (c) Interfacial alignment between hBN and 6P molecules in the 6P($-6.29$) plane. A theoretical tilt angle of the needle growth direction with hBN’s zigzag direction is obtained (dark molecules are at the interface, brighter ones are on top).](image)
been found as can be seen in the AFM image in figure 8(b). conjugated molecules very, similar growth patterns to 6P have the substrate facilitating optical microscopy. Average lateral enhance the optical contrast between DHTA7 crystallites and identified (see FFT image in figure 8(c)). According to DFT calcul-

\[ \begin{align*}
\text{molecular arrangement at the DHTA7/hBN interface is prepared. Based on the latter argumentation a tentative model of the molecular arrangement at the DHTA7/hBN interface is presented in figure 8(a). The in-plane hydrogen bonds enforce a rather planar molecular arrangement with poor in-plane orbital overlap but increased } \pi-\pi \text{ stacking with subsequent layers as also observed for related systems } [98]. \text{ According to DFT, a unit cell contains four molecules whereas the individual molecules are tilted by } \approx 8.5^\circ \text{ with respect to the DHTA7 } (001) \text{ plane (figure 6(b)) which is considered to be also the present contact plane with hBN. In this case, the angle between long molecular axes and the long needle axis should be } \approx 79^\circ. \text{ Optical microscopy with linearly polarized light strongly indicated that the needles were single domains. Taking into account that light absorption is strongest when the polarization direction of the incident light matches the long molecular axis, a relative orientation angle between the long needle axes and the long molecular axes of } (79 \pm 3)^\circ \text{ could be deduced, in agreement with the theoretical predictions. Since the orbital overlap in needle growth direction is very weak, also the electrical conductivity along the needle is extremely low. Therefore, charge transport in the needles was studied using electrostatic force microscopy (EFM) } [205]. \text{ In the dark, charges deposited via the biased AFM tip stayed localized around the charging point whereas under illumination charges spread out through the needle network revealing photoconductivity. Since the light absorption was depending on the light polarization, directional charge movement could be stimulated. Only those needles in the network became photoconductive that contained molecules whose long molecular axes matched the polarization direction. In order to quantify the conductivity along the needles, time dependent EFM measurements on single needle field effect devices were carried out. The field effect devices were realized by transferring graphite flakes as contact electrodes onto the hBN flakes prior to DHTA7 deposition. That way, resistivity values in the order of } \approx 1 \times 10^9 \Omega \text{m in the dark and } \approx 3.5 \times 10^7 \Omega \text{m under illumination were found. The low conductivity along needle direction was in accordance with the growth model and the poor orbital overlap between adjacent molecules.} 
\end{align*} \]

**Hexacontane on exfoliated hBN**

The adsorption of the linear, long chain alkane hexacontane \((C_{60}H_{122})\) on exfoliated hBN was investigated utilizing high resolution AFM [184]. The adsorption of low cost, non-toxic...
Figure 9. Hexacontane on exfoliated hBN. AFM images of hexacontane on hBN at different scales. Scale bars: (a) 100 nm, (b) 5 nm, (c) 1 nm. (c) The transition between the hexacontane layer and hBN substrate. (d) Adsorption model with alignment along the zigzag direction. Reproduced from [184]. CC BY 4.0.

Figure 10. Adsorption model of Hexacontane and Diacetylene on hBN. (a) Experimentally verified model for the adsorption and ordering of hexacontane on hBN. (b) Speculative alignment of 10,12-nonacosadiynoic acid (diacetylene compound) on hBN with alkyl chain alignment along the zigzag direction. (a) Reproduced from [184]. CC BY 4.0. (b) Reproduced from [81]. © IOP Publishing Ltd. All rights reserved.
alkanes is of interest in the fields of catalysis [206], surface passivation [207], and lubrication [208], but they are also interesting systems to study supramolecular assembly [209]. Hexacontane films were prepared either by vapor deposition in high vacuum or from solution. From the monolayer morphology, a flat lying molecular orientation was deduced. The monolayer morphology revealed from AFM measurement shown in figure 9 consisted of parallel rows with a period of (7.9 ± 0.2) nm (see figure 9(b)) and the measured periodic corrugation along the rows yielded (4.4 ± 0.02) nm very close to the molecular spacing found in the bulk crystal [80, 210]. Further, it turned out that the individual molecules align with their long axes parallel to hBN’s zigzag direction (see figures 9(c) and (d)), which was also supported by molecular mechanics simulations and is consistent with x-ray investigations [211]. A structural model is provided in figure 10(a).

Adsorption and ordering on transferred CVD hBN. So far, the discussion focused on the adsorption, growth, and self-assembly of molecules on exfoliated hBN nano and micro flakes. Similar studies—although at much smaller extend—have been performed on CVD grown hBN transferred to SiO2/Si substrates. These systems are of special technological interest since CVD hBN has the potential to be used in scalable processes.

C60 on transferred CVD hBN

Maybe, the simplest molecule to use is C_{60}, which behaves isotropic due to its spherical symmetry. In fact, C_{60} based OFETs with mobility values up to $\mu \sim 2.9$ cm$^2$ V$^{-1}$ s$^{-1}$ and on/off ratios of 10$^4$ have been realized on CVD grown single layer hBN transferred to a SiO$_2$/Si substrate [49]. In this case, hBN was used to decouple the C$_{60}$ film from the SiO$_2$. The insertion of the hBN interface layer increased the mobility by a factor of ~40 compared to C$_{60}$ films directly grown on SiO$_2$. The superior charge transport properties were attributed to the epitaxial 2D growth of C$_{60}$ on hBN. C$_{60}$ films with a nominal thickness of 20 nm were thermally evaporated at a substrate temperature of 383 K and a rate of 0.02 nm s$^{-1}$. AFM measurements revealed 100–200 nm large terraced grains with a typical step height of ~0.8 nm, which fits well to the height of a single C$_{60}$ layer. Significantly smaller grains without noticeable step structure were found on a reference film grown under identical conditions on a bare SiO$_2$ substrate. Further, the film roughness was much higher on SiO$_2$ than on hBN. From TEM and SAED measurement of C$_{60}$ films deposited onto TEM grids with hBN as shown in figure 11, confirmed an epitaxial relationship between hBN and the C$_{60}$ film. Additional grazing incidence x-ray diffraction investigations clearly revealed that the (1 1 1) planes of the face centered cubic C$_{60}$ crystals were aligned parallel to the hBN surface and confirmed the 2D close structure of the C$_{60}$ films which indicates a 2D, layer-by-layer growth facilitated by the vdW interaction between C$_{60}$ and CVD hBN. Further, it was found that the C$_{60}$ crystal edges typically align either 10° or 26° off the hBN zigzag direction. Calculations of the most stable orientation performed via DFT calculations including vdW dispersion forces yielded consistent results with the experimental observation predicting the most stable orientations with the C$_{60}$ crystal edges aligned 9°–12° and 21°–25° with respect to the hBN zigzag directions (see structural model in figures 11(a) and (b)).

2D molecular self-assembling on exfoliated hBN. Besides compact organic semiconductor layers also single layer or multilayer self-assembled organic layers and networks have been realized on exfoliated hBN.

Diacetylene self-assembled monolayer on exfoliated hBN

The formation of self-assembled monolayers of diacetylene has been demonstrated on atomically flat exfoliated hBN sheets [81, 212]. In this case, 10,12-nonacosadiynoic acid diacetylene molecules were brought into solution with xylene and spin coated on the hBN/SiO$_2$/Si substrates. AFM characterization of the SAMs on hBN revealed long parallel stripes corresponding to self-assembled molecular rows of flat lying molecules with a stripe period of (7.6 ± 0.2) nm. For the molecular arrangement, a model was suggested where molecules group in pairs such that the carboxy end groups of one chain face those of the neighboring chain [81]. Further, it was suspected that the alkyl chains of the molecules align with one of the main crystal axes of the hBN lattice [81, 211]. Based on the idea that the alkyl chains tend to align with the zigzag direction as confirmed for hexacontane [184], we suggest a tentative structural model which is provided in figure 10(b).

Unlike substrates as HOPG or MoS$_2$ where domain sizes were only in the few 100 nm range, on hBN single domains—a few $\mu$m in size—were found. This was attributed to a reduced nucleation density due to the exceptional large area flatness of hBN. It was noted that for the self-assembling of the diacetylene molecules single atomic steps of the substrate might be sufficient to interrupt the process. In addition, on these substrates also on-surface photopolymerization of the SAM to polydiacetylene was successfully performed. It was also found that the polymerization rate was two orders of magnitude higher than for graphite, which was attributed to the large difference between the hBN band gap (~5.9 eV [37]) and the excitation energy of the diacetylene (~3.1 eV).

PTCDI/melamine and CA/melamine self-assembled networks on hBN

Nanoporous networks formed from perylene tetra-carboxylic di-imide (PTCDI) and 1,3,5-triazine-2,4,6-triamine
Covalent organic frameworks on exfoliated hBN

Multilayers of covalent organic frameworks (COFs) on exfoliated hBN transferred to SiO2/Si or HfO2/Si were selectively grown by a solvothermal process using TAPP and TAP precursors [107]. The work was motivated by the fact that layered 2D COFs represent planar π-conjugated systems with well-ordered stacking, which can result in exceptionally high charge carrier mobilities [216, 217]. Further, theoretical work...
predicts a minimum perturbation of the electronic band of the active layer on the hBN support [218] making intrinsic properties accessible. The presence of 5–8 monolayers of the COF was deduced indirectly from Raman and fluorescence measurements and has been complemented by XPS, UV–VIS–NIR absorption spectrometry, and AFM. A comparison of the Raman spectra of the COF and the corresponding precursors revealed that the aldehyde stretching vibration bands related to TPA at 1691 cm\(^{-1}\) and 1702 cm\(^{-1}\) were missing in the film. Further, two bands at 1570 cm\(^{-1}\) and 1625 cm\(^{-1}\) appeared that were attributed to the C = N bond stretching vibration between the phenyl groups of TPA and TAPP. These trends were considered as indication for an imine-connected structure. The presence of a C = N bond was additionally confirmed by XPS. A model of the formed network can be found in figure 12. Statistical evaluation of AFM topography films before and after COF deposition yielded a COF film thickness in the range between ~2.3 and ~4.6 nm on the ~40 nm thick (~120 layers) hBN flakes.

2D porphyrine arrays on exfoliated hBN

The fluorescence properties of 2D supramolecular networks of 5,10,15,20-tetrakis(4-carboxylphenyl)porphyrine (TCPP) solution deposited onto exfoliated hBN/SiO\(_2\)/Si have been studied [68]. The adsorbate-substrate vdW interaction caused a clear red-shift of the TCPP fluorescence. The hBN flakes were obtained by exfoliation from hBN single crystals and had typical lateral dimensions of 20–100 µm and exhibited thicknesses between 20 and 100 nm which corresponds to 60–300 hBN layers. After immersing the hBN/SiO\(_2\) substrate for 10 s into a 13 µM ethanol TCPP solution, AFM images revealed the existence of about ~0.26 nm high islands with typical lateral extensions of 50–100 nm. The observed island height suggested that the TCPP molecules adsorbed flat lying with their porphyrine macrocycle oriented parallel to the surface. High-resolution AFM images revealed two distinct TCPP phases with square and hexagonal symmetry, respectively. The square lattice had a lattice constant of \(\alpha \approx 2.22\) nm, whereas the hexagonal lattice had one of \(\alpha \approx 4.37\) nm [68]. However, the hexagonal structure turned out to be unstable and disappeared within ~1 d. A model of the stable square lattice arrangement can be found in figure 12. The observed structures were modeled by hydrogen bonded junctions of two or three carboxylic acids for the square and hexagonal phases, respectively. Corresponding DFT calculations strongly supported this model and estimated the binding energies per molecule to be 2.30 eV for the square lattice and 0.68 eV for the hexagonal lattice in agreement with the observed stability of the phases [68]. However, more refined calculations using DFT including dispersion corrections [178] revealed a deformation of the porphyrine macrocycle upon adsorption on hBN resulting in a bowed geometry of the molecules. This was attributed to the aryl side groups, which cannot adopt a coplanar alignment with the porphyrine macrocycle and lift up the plane of the macrocycle resulting in a small gap between molecule and substrate. Driven by vdW forces, the macrocycle can flex and bow down towards the gap adopting the bowed geometry. A direct consequence of the non-planar conformation of the porphyrine macrocycle is a red-shift in the Soret and Q-band fluorescence of the molecule [219].

Adsorption and ordering on metal supported hBN nanomesh substrates

A very active field of research is studying 2D molecular self-assembly and ordering on metal supported hBN substrates. The ability to immobilize small entities in ordered 2D structures might be the basis for functional surfaces in molecular electronics, selective catalysis or advanced data storage. In this light, especially molecular arrangement on epitaxial hBN nanomesh templates have been explored. The insulating hBN can be used to minimize the electric coupling between molecules and metal substrates, providing the opportunity to study the intrinsic molecular properties. A site specific adsorption on hBN nanomesh substrates has been demonstrated amongst others for molecules like C\(_{60}\) [52], naphthalocyanine (Nc) [54], (metal)-phthalocyanines (MPc) [55, 125, 220, 221], porphine (2HPC), tetracyanoquinodimethane (TCNQ) [57], hexaiaoicyclohexa-m-phenylene (I\(_2\)CHP) [75], pentacene (5A) [72], etc… [50].

While molecules adsorbing on transferred hBN (exfoliated or CVD grown) find an atomically smooth surface they find quite a different situation on metal supported epitaxial hBN. The interaction with the metal substrate induces a mesh-like geometrical and/or electrical corrugation of the hBN which can effectively trap molecules. Basically all molecules under test showed site specific adsorption on hBN nanomesh substrates, yielding ordered arrays which can act as intermediate for molecular networks. At low coverages adsorption within the nanomesh pores is often preferred. However, usually the molecules avoid the pore center and tend to adsorb at off center positions towards the pore rim. The strong tendency of molecules and atoms to adsorb in the hBN nanomesh pores is attributed to polarization induced trapping [220]. The pores and wires of the hBN nanomesh represent regions which are closely bound (pores) and loosely bound (wires) to the metal support, respectively. On the one hand, the site-selective bonding of the hBN nitrogen atoms to the metal substrate atoms causes a more [54] or less [145] strong geometric corrugation of the hBN layer, and on the other hand it also leads to an electronic corrugation in terms of periodic work function modulations [57, 220]. Thus, one obtains holes of low work function surrounded by high work function wires, which can be described as dipole rings. At the transition between pore and wire, significant electric fields can prevail that will interact with atoms and molecules adsorbed on the hBN surface [220]. Thus, induced or permanent dipoles in molecules are attracted to the high potential gradient which enhances immobilization there. In the following three examples of molecular adsorption and growth on hBN nanomesh substrates are presented for the purpose of comparison to transferred hBN substrates.
Historically, the first adsorption experiments on an hBN/Rh(111) nanomesh were performed using C$_{60}$ fullerenes [52]. However, in this case no systematic study from low to high coverages were conducted. Therefore, no explicit prove was provided that the C$_{60}$ molecules are initially trapped in the pores. Nevertheless, well ordered structures—closely following the nanomesh topography—were reported. According to STM measurements, the nanomesh wires were nicely decorated by C$_{60}$ whereas the very pore center stayed often—but not always—unoccupied. That might be interpreted as preferred off center adsorption as well. The C$_{60}$ spacing along the wires was around ~1 nm. 1 nm nearest neighbor distance was also found on C$_{60}$ monolayers on hBN/Ni(111) [67]. They were obtained by thermal desorption of multilayers and formed a commensurate hexagonally closed packed ($4 \times 4$) structure. This is consistent with the molecular spacing in the fcc C$_{60}$ (111) plane, which was also found for C$_{60}$ adsorbed on CVD grown hBN on SiO$_2$/Si [49]. In this respect, metal supported hBN seems to be similar to transferred hBN. However, geometrical and electrical corrugation might vary quite significantly for different metal supports, which also might lead to different adsorption geometries.

5A on hBN/Rh(111)

C$_{60}$ is a molecule noticeably smaller than the nanomesh pore but isotropic due to its spherical shape. An interesting example to compare is the 5A molecule, which is also significantly smaller than the nanomesh-pores but anisotropic due to its rod-like shape. On hBN/Rh(111), 5A initially adsorbs flat lying and is preferentially located in the pores [72]. The electric field at the pore-wire transition attracts the 5A molecules causing them to arrange along the pore rim. However, the 5As adsorb preferentially with their long axes facing an intersection of the wires and never adsorb parallel to the wires. That way, six molecules can arrange along the pore perimeter forming a six-fold geometry, which is not found for 5A on exfoliated hBN [14, 65]. However, defects or adsorption of multiple 5As in the same valley can cause other adsorption geometries [72]. Increasing the 5A coverage beyond 0.2–0.3 ML yields a transition from flat lying molecules to an upright configuration, as has been indicated by NEXAFS [165]. Accompanied with increasing film thickness also changes in the C1s photoemission peak have been observed, which were attributed to originate entirely from the gradual rearrangement from flat-lying to upright 5A configuration. On exfoliated hBN flat lying molecules formed a compact interface layer on which the succeeding layer grew in an upright fashion [14]. Further investigation with micro-energy electron diffraction and STM on a ML thick island grown at room temperature confirmed an almost upright standing arrangement in the typical herringbone motif as frequently found for rod-like conjugated organic molecules [32, 94, 96, 222]. However, the influence of the hBN nanomesh corrugation on the resulting 5A structure appeared to be strong. Even, though the typical herringbone structure was adopted, the lattice parameters and unit cell angles deviated noticeably from the 5A bulk [223] arrangement. Since organic structures—primarily bound by vdW interactions—are pliable, it appears likely that the geometric and electrostatic corrugation of the hBN nanomesh can sufficiently modify the film in order to achieve best match with the substrate. A flat-lying to upright transition is very typically for rod-like aromatic molecules in case of weakly interacting amorphous, contaminated, or strongly corrugated surfaces. Going upright, forming herring-bone packed islands in, or close to the herringbone bulk structure is a general trend and is closely related to the possibility to form an ordered, compact wetting layer [10, 32, 97, 222, 224, 225]. Apparently, the corrugation of the nanomesh is sufficient to enforce the upright molecular configuration form the first layer on without forming a flat-lying interface layer.

Naphthalocyanine on hBN/Rh(111)

5A and C$_{60}$ are examples of molecules which are smaller than the nanomesh pores allowing for multiple adsorption within a single pore. In contrast, Nc is almost as large as a pore (~2 nm), consequently only single occupation is possible. On hBN/Rh(111), a highly selective adsorption in the pores was observed for vapor deposited Nc at room temperature [54]. The distance between the pores was large enough.
to suppress molecule-molecule interaction between adjacent occupied pores. Therefore, ordering was fully dominated by the molecule-substrate interaction. This way, a well ordered array of Nc molecules was realized with the periodicity of the nanomesh (~3.22 nm). In contrast, on atomically smooth hBN a significant influence of intermolecular interaction on the ordering can be expected.

Summary/conclusions

Since the realization of mechanically exfoliated Gr [120] as first representative of 2D materials, the family of 2D vdW materials has grown [226, 227], and the concept of exploiting the vdW nature of these surfaces for growth and the fabrication of vdW heterostructures has attracted huge interest [228, 229]. hBN turned out to be best suitable as vdW substrate for the growth of high quality organic semiconductor thin films enabling access to the intrinsic properties of the organic layers with minimum interference of the interface. This way, using exfoliated multilayer hBN as gate dielectric, record field effect mobilities in the order of μ ~ 30 cm² V⁻¹ s⁻¹ for C₈-BTBT [104, 106], μ ~ 11.5 cm² V⁻¹ s⁻¹ for rubrene [161], and μ ~ 1.6 cm² V⁻¹ s⁻¹ for 5A [14] have been realized. Further, atomically thin CVD hBN transferred to SiO₂ served as vdW interface layer in C₆₀ FETs yielding a field effect mobility of μ ~ 2.9 cm² V⁻¹ s⁻¹ [49]. The exceptional performance can be explained by the properties of the vdW interface between hBN and the organic thin film. First, hBN is atomically smooth and homogeneous which drastically reduces nucleation events [49, 81, 230]. Second, the vdW interaction between hBN and the organic molecules is weak and typically affects only the first one or two layers [14]. The subsequent layers already adopt their bulk equilibrium structure. In addition, the intermolecular interaction is often also dominated by vdW forces making the material ‘soft’, and strain can be accommodated more easily [231]. Therefore, also mismatched systems can grow rather large domains. Third, there are no dangling bonds on the hBN surface which could lead to structural/chemical distortion and charge trapping at the interface. Further, the low dielectric constant of hBN (ε = 3–4 [40, 41]) reduces polaronic coupling which is also a source of mobility reduction [14]. Even though the interaction between hBN and the organic layer is weak, it seems sufficient to establish an epitaxial relationship between substrate and organic crystalline thin film. Specific molecular alignment with the hBN substrates has been reported for several systems. The linear molecules 5A [14], DHTA7 [204], and hexacontane [184] preferentially adsorb with their long axes parallel to hBN’s zigzag direction, whereas 6P [12] aligns parallel with the armchair direction. An alignment with a high-symmetry direction of hBN was also suspected for the adsorption of diacytene [81, 212]. For molecules containing long alkyl chains a general trend for adsorption along the hBN’s zigzag direction might be expected. In case of 6P and DHTA7 the initial alignment resulted in epitaxial needle-like crystal networks with specific discrete growth directions. Also hexacontane formed epitaxially aligned rows on hBN, whereas 5A [14] and C₈-BTBT [104, 106] preferred an upright molecular orientation even though the interface layer consists of flat-lying molecules. Apparently, even though an epitaxial configuration is adopted at the interface an epitaxial continuation for the upcoming layers is not guaranteed. An epitaxial 3D growth of the organic layer is only possible if the interface configuration is sufficiently close to a bulk plane as is the case for 6P [12] and DHTA7 [204] but also for self-assembled covalent organic networks formed by TAPP and TPA [107] and hydrogen bond stabilized melamine based networks [108, 109]. The desired perfect substrate/thin film decoupling resulting in a quasi-free standing organic layer is not automatically fulfilled, especially for single layer films. For example, the fluorescence spectra for sub-monolayer TCPP on exfoliated hBN are red-shifted due to a vdW induced deformation of the molecule’s porphyrine macrocycle [68]. In case of 5A [14] and C₈-BTBT [104], the formed interface layer comprised of flat lying molecules seems to be responsible for efficient decoupling. Even though the introduction of atomically thin hBN sheets as vdW interface layers between organic thin film and substrate was demonstrated [49], a complete decoupling is not guaranteed for very thin hBN. For example, the morphology and ordering of 6P needles on exfoliated hBN/SiO₂/Si depends on the hBN thickness [12]. For hBN flake thicknesses below three layers ordering degraded significantly. On the one hand, corrugations of the SiO₂ surface can be transferred through the very thin hBN, and on the other hand, electric screening from dipole fields arising from trapped water at the hBN/SiO₂ interface might be incomplete. A significant effect of the support is evident in metal supported epitaxial monolayer hBN. hBN/metal support interactions often result in nanomesh structures [54] which are morphologically and electrically corrugated providing preferential trapping of molecules in the nanomesh pores [50, 54, 72].

Ultrathin hBN has proven to be a useful vdW substrate for the growth of high-quality organic crystalline films. The weakly interacting substrate enables the exploration of organic thin film properties in the intrinsic limit, which is extremely valuable for the improvement of organic semiconductor devices but also for the investigation of fundamental questions. Improved fabrication and transfer methods of single and multilayer hBN—certainly developing in the near future—together with the virtually unlimited diversity of organic compounds will pave the way for vdW/organic heterostructures with designed mechanical, electrical, optical and chemical properties.

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