Layer Dependent Wetting in Parahexaphenyl Thin Film Growth on Graphene*

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(Received 28 November 2013; Accepted 15 January 2014; Published 8 February 2014)

In order to exploit graphene (Gr) as a transparent electrode in organic optoelectronics, a profound understanding of molecular wetting and diffusion processes on this material is essential. Properties of Gr like band structure, work function, or elasticity depend significantly on the layer number. Here, we report on Gr layer dependent differences in the growth morphologies of hot wall epitaxy deposited sub-monolayer thin films of the one-dimensional conjugated parahexaphenyl (6P) molecule on exfoliated Gr/SiO₂. At deposition temperatures around 363 K, 6P forms straight needles arranged in regular networks on single layer graphene. Within the first four Gr layers, the average needle height increases and the average needle length decreases thereby reducing the specific 6P-Gr interface area. The variations in morphology and wetting behavior with the Gr layer number arise from changes in the growth kinetics induced by differences in adhesion and diffusion properties with Gr thickness. [DOI: 10.1380/ejssnt.2014.31]

Keywords: Atomic Force Microscopy; Growth; Wetting; Scanning Tunneling Microscopy; Pb; Si(111)

I. INTRODUCTION

Graphene (Gr) is one of the most prominent materials currently investigated. Experimental work which essentially started in 2004 [1] brought forth exceptional intrinsic properties of Gr like extremely high electron mobility [1], enormous mechanical strength [2], and impermeability to gases [3]. Researchers and engineers try to exploit these extraordinary properties for pushing forward the basic understanding of transport phenomena like quantum hall effect [4, 5] and Klein tunneling [6] on the one hand, and relevant technological applications like high frequency transistors [7] or transparent electrodes [8] on the other hand. Recently, Gr has also been investigated towards the possibility to create surfaces with tunable wettabili[10–12]. Contradictory results and interpretations of the findings triggered a discussion about Gr thickness dependent wetting properties of water [13–15]. An answer to the question of Gr layer dependent wetting is not only relevant for applications of interfaces between graphitic carbons and liquids - as used in electro-chemical storage devices like batteries or supercapacitors - but is also fundamental for the control of thin film growth. For instance, deposition of Au or Ag on few layer Gr (FLG) and subsequent annealing yielded nanoparticles increasing in size with Gr layer number [16–18]. These observations were attributed to layer dependent changes in the adatom adhesion and diffusion properties caused by quantum size effects [16].

Thin film growth control is also a central issue in organic electronics [19], because the intrinsic film properties as well as the formed interfaces significantly determine the device performance [20–22]. Especially, the use of Gr as possible transparent and mechanically flexible electrode for organic light emitting diodes (OLED) and solar cells demands for a fundamental understanding of the behavior of organic compounds on Gr substrates [8]. An intensively studied model system for organic thin film growth on solid surfaces is parahexaphenyl (6P) [23–30]. The rodlike, conjugated 6P molecule (C₃₆H₂₄) crystallizes in a herringbone bulk structure [31] and exhibits a gap of ∼3.1 eV between its lowest unoccupied molecular orbital and the highest occupied molecular orbital which makes it suitable for OLED applications [22]. So far, a few studies have been dedicated to the growth of 6P on Ir(111) supported Gr [32, 33]. There, wrinkles [34] - always present on Gr grown by chemical vapor deposition - play an important role in the nucleation of 6P crystallites [35, 36]. In a previous work, we investigated the temperature dependence of 6P growth morphologies on SiO₂ supported exfoliated Gr [37]. Exfoliated Gr is wrinkle free and offers the possibility to study homogeneous nucleation. Around 363 K, we observed variations in 6P morphology that seemed to depend on the Gr layer number. Here, we examine this observation in more detail and discuss the phenomenon in the framework of Gr layer dependent surface energies, 6P wetting, and diffusion behavior.

II. EXPERIMENTAL

The Gr samples were prepared by mechanical exfoliation [1] of kish graphite (NGS Naturgraphit GmbH) on silicon wafer pieces ∼1×2 cm² (IDB technologies Ltd) with 300 nm thermally grown silicon oxide. The samples were inspected visually by optical microscopy and micro-Raman measurements to confirm the presence of single layer graphene [38]. The 6P deposition was carried out by hot wall epitaxy (HWE) [39, 40] at a base pressure of ∼5×10⁻⁶ mbar. In order to reduce the amount of adsorbed water and other volatile adsorbates that might have contaminated the surface, the samples were heated in vacuum for 10 min at 393 K. The sample temperature was adjusted via resistive heating. A source temperature of 510 K and a slightly higher wall temperature of 520 K

*This paper was presented at the 12th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSSIN-12) in conjunction with the 21st International Colloquium on Scanning Probe Microscopy (ICSPM21), Tsukuba International Conference Center, Tsukuba, Japan, November 4-8, 2013.

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were chosen for 6P deposition. The obtained 6P coverages, given in the portion of the SiO$_2$ substrate covered with a single layer of upright standing 6P molecules was $\sim 63\%$. Since the HWE chamber was not equipped with a deposition monitor, the deposition time was calibrated by measuring the obtained 6P coverage of SiO$_2$ test samples and was typically $\sim 2 - 5$ min.

AFM measurements were carried out by using an Asylum Research MFP-3D system equipped with a closed loop scanner ($80 \times 80 \mu m^2 \times 15 \mu m$). For the topography measurements, the AFM was operated in intermittent contact mode under ambient conditions using NSG30 and NSG10 silicon probes from NT-MDT (typical tip radius $< 7$ nm and force constants of $\sim 40$ N/m and $\sim 12$ N/m, respectively). Simultaneously to the topography images, the corresponding AFM phase images were recorded. In AFM phase imaging, the difference of the phases between the oscillating cantilever and the driving piezo is measured. The phase difference depends on the local AFM tip - surface interaction and is thereby influenced by the adhesion, repulsion, or friction between tip and surface but also by the viscoelastic response of the substrate material [41]. In order to avoid damaging of the soft 6P films, the AFM feedback was set to “soft tapping” conditions, therefore, operating mainly in the attractive tip-sample interaction regime. Further, a tip decoration by 6P molecules during the scans is likely which makes the system especially sensitive to 6P-substrate interactions. Under the applied conditions we assume that the phase primarily provides information about the local adhesion forces.

III. RESULTS AND DISCUSSION

6P molecules deposited on graphene surfaces form - dependent on the substrate temperature - two different kinds of morphologies: islands consisting of molecules with their long molecular axes oriented roughly perpendicular to the surface, and needles composed of molecules with their long axis parallel to the substrate surface [37]. In the following and throughout the manuscript we will term structures consisting of molecules with their long axis parallel to the surface as needles, and those composed of upright standing molecules as islands. The evolution of morphology with increasing substrate temperature is observable in Fig. 1, showing a series of AFM topography images for deposition temperatures from 333 K to 393 K. For a deposition temperature of 333 K islands and needles coexist on the Gr flake (Fig. 1 a)). It is evident from Fig. 1 a), where single layer graphene (SLG) and double layer graphene (DLG) are present, that there is no dependence of the morphology on the Gr layer number. The needles’ long axes seem to be preferentially aligned along discrete growth directions with $\sim 60^\circ$ relative orientation angles to each other. Additionally, a slight decoration of the Gr-Gr step edge with needles can be observed. The uniformly distributed, blot-like structures of constant height ($\sim 2.5$ nm) are single layer 6P islands. The islands overgrow the Gr-Gr step edge undisturbed and do not seem to nucleate preferentially at the step edges (neither SiO$_2$-Gr nor Gr-Gr).

When the deposition temperature is increased to 363 K (Fig. 1 b)), only needles are found on the Gr, whereas on the SiO$_2$ still just single layer islands exist. In the presented image, SLG as well as three layer Gr (3LG) and four layer Gr (4LG) are present. The needles do neither overgrow the Gr-SiO$_2$ step edges nor the Gr-Gr step edges. No preferential step edge decoration is present. Compared to the 333 K sample, the needle size - especially the needle length - has significantly increased.

Raising the deposition temperature to 393 K (Fig. 1 c)), results in extended well defined, and straight needles that overgrow the Gr-Gr step edges undisturbed but still do not overgrow the SiO$_2$-Gr rim. Here, again discrete needle growth directions oriented by $\sim 60^\circ$ to each other.
can be found.

While the films grown at 333 K and 393 K are homogeneous over the whole Gr flake, the situation is different for 363 K deposition temperature. In Fig. 2 a), a 50×50 μm² AFM topography image of a 6P film deposited at 363 K is presented. The film on the Gr flake consists exclusively of large needles. In Fig. 2 a) it is well visible that the regions of uniform morphology are usually sharply confined. In addition, these regions show a change in the corresponding AFM phase of the Gr substrate. In Fig. 2 b), the corresponding phase image measured simultaneously with the topography (Fig. 2 a)) is presented. In most cases, different 6P morphologies and different phase contrasts can be simply assigned to different numbers of Gr layers. However, different film morphologies are also found for adjacent areas which are of the same height, and therefore have the same assigned Gr layer number. Such a case can be seen on the large central part of Fig. 2 a) that was assigned to be DLG. There, the morphology changes from 10 μm long straight needles in the center of the image to much smaller, starlike arrangements at the top of the image. In the phase image (Fig. 2 b)) a gradual change of the phase contrast on Gr from center to top, roughly corresponding to the change in 6P morphology, is observed.

The AFM topography and phase images presented in Fig. 3 provide more details about the different film morphologies. The 4LG, the 6P islands, and the SiO₂ substrate appear brightest in the phase image Fig. 3 b), whereas SLG and DLG are darker on average. The corresponding line profiles along the green and magenta lines in Fig. 3 a) and 3 b) are depicted in Figs. 4 a) and 4 b). Even though there is a clear height difference between SLG and DLG in the height profile along the green line in Fig. 3 a), the phase contrast is almost zero (black line in Fig. 4 a)). Opposite to that, the line profiles along the pink line in Figs. 3 a) and 3 b) depicted in Fig. 4 b) do not show any height difference between the graphene layers denoted SLG and SLG-II but exhibit a noticeable phase difference. Additionally, the 6P film morphology on SLG-II differs noticeably from SLG. In Fig. 4 c), topography line profiles taken on all different areas along the red, yellow, cyan, and orange scan lines (indicated in Fig. 3 a) are depicted. The slope of the 6P needle profiles are similar for all areas. However, there is a clear trend that the longer, well defined needles on the SLG and DLG exhibit a smaller height (typically 10-15 nm) compared to the shorter needles found on the SLG-II (typically 15-20 nm) and on 4LG (typically 20-40 nm) areas. This indicates a higher wettability of SLG and DLG compared to thicker Gr substrates.

In general, 6P strongly tends to form 3D crystals with herring bone bulk structure. Even on a high energy surface like the SiO₂ substrate (78SiO₂ = 70-80 mJ/m²) [42], 6P wetting is unfavorable, especially, because the dispersive contribution to the SiO₂ total surface energy is max. 30%. The low index 6P plane with the lowest surface energy is the 6P(001) plane (γ6P(001) = 107 mJ/m²) [43]. In order to maximize the 6P(001) surface area it is necessary to form islands of almost upright standing molecules whose top surface is - depending on the molecular tilt angle with respect to the surface - close to the 6P(001) surface. Since the cohesive energy per 6P molecule in the bulk is ~ 3 eV [43], the formation of multilayer islands should be expected in order to minimize the surface to volume ratio and therefore further minimizing the total free energy. On SiO₂, this is never observed within the applied temperature range and the time scale of the experiment. Indeed, Yang et al. [44] observed the formation of 6P bilayer islands on SiO₂ upon annealing at 200 C° for 1.5 h. This indicates that the formation of the energetically most favorable, bulk-like multilayer 6P islands is kinetically hindered due to significant diffusion barriers across the island rim [23].

In contrast to the SiO₂ substrate, there is a strong tendency to form needles on Gr. The coexistence of both
morphologies at temperatures below 363 K suggests that both configurations are energetically similar. The literature values of the Gr free surface energy are in the range of \( \sim 30-50 \text{ mJ/m}^2 \) which is considerably lower than that of SiO\(_2\) [45, 46]. However, while the dispersive component of the SiO\(_2\) surface energy is minor [42], that of Gr is much more prominent [47]. 6P is a hydrocarbon whose intermolecular interaction is dominated by dispersive (Vander-Waals) forces. Nevertheless, there is also a small, but important electrostatic contribution originating from negative electric charges on the carbon rings equilibrated by positive charges on the hydrogen atoms. This electrostatic contribution is finally the cause for the formation of the herring bone bulk structure [48, 49]. Based on simple surface energy considerations, one should expect 6P growing on Gr in the same mode as on the SiO\(_2\) substrate.

This is indeed partially observed for low deposition temperatures [37] but in contradiction to the observations at higher deposition temperatures. Usually, the adsorption energy of a single lying 6P molecule is considerably higher than that of an upright standing one. Therefore, it is generally accepted that 6P always adsorbs and diffuses flat lying and that the initially formed small clusters also favor the lying configuration. Just upon a critical cluster size, the upright standing configuration becomes energetically more favorable [50]. The critical cluster size for the transition from lying to upright standing molecular orientation strongly depends on the molecule-substrate in-

FIG. 3: 10×10 \( \mu \text{m}^2 \) detail from the bottom right in Fig. 2 (6P deposited @ 363 K). Topography image a) (z-scale = 10 nm) and the corresponding phase image b) (z-scale = 20°). The phase contrast in b) is exaggerated for better visibility.

FIG. 4: Line profiles taken along the lines indicated in Fig. 3. The dark line profiles correspond to the phase and the colored correspond to topography. The fat black horizontal lines indicate the Gr layers and the cross hatching symbolizes the SiO\(_2\) substrate. The height differences in a) correspond to 1, 2 and 3 Gr layers. In b) no height difference between SLG and SLG-II is detectable, but there is a clear difference in the phase indicating different mechanical/adhesive properties. In c) height profiles across 6P needles on a different number of Gr layers are depicted.
teraction. The interaction between the Gr and the 6P is strongly influenced by $\pi - \pi$ stacking interactions which are not present on the SiO$_2$ surface. A rough estimation of the binding energy according to Björk et al. [47] yields $\sim 2.6$ eV per 6P molecule lying flat on the Gr. Therefore, lying molecules are more favorable on the Gr than on the SiO$_2$. The fact that the observed needles coexisting with the islands on the 333 K sample (Fig. 1 a)) exhibit preferential growth directions indicates that there exist energetically more favorable adsorption geometries which stabilize the needles. Therefore, the islands consisting of upright standing molecules are just metastable configurations since the global energetic minimum is adopted in the needle phase.

The interesting changes in the 6P film morphology observed at 363 K arise from differences in the growth processes determined by the layer dependence of the Gr surface energy, 6P adsorption geometry, and diffusion properties. An indication for layer dependent changes in the surface energy is provided by the AFM phase images. The phase is mainly sensitive to the local tip-substrate adhesion and the viscoelasticity of the substrate material [41]. To avoid damage of the soft 6P film, the AFM feedback was set to operate mainly in the attractive tip-sample interaction regime. Additionally, a tip decoration by 6P molecules during the scans is likely which makes the system sensitive to 6P-substrate interactions. We assume that in this case the phase is primarily sensitive to the local adhesion forces. Due to the close relation between adhesion force and surface energy [51–53], the phase image also identifies differences in surface energy. A further indication for a surface energy related phenomenon is the fact that the specific Gr-6P interface area decreases with increasing Gr layer number. The specific interface area and island boundary length are depicted as a function of the Gr layer number in Fig. 5. Obviously, the 6P wetting becomes more and more unfavorable as the number of underlying Gr layers increases.

However, a variation of the Gr surface energy with layer number is still under debate. Some groups found an impact on the wetting properties of water depending on the substrate and the Gr layer number as a result of wetting transparency [10–12]. Other researchers deduced, based on a thermodynamic model and molecular dynamics simulations, decreasing water contact angles for the first 3 layers of unsupported Gr [13]. In contrast to that, further groups found that the water contact angles are essentially independent from the support as well as from the number of Gr layers and are the same for highly oriented pyrolytic graphite (HOPG). Deviations of the contact angles measured on Gr from those of HOPG were attributed to defects in the Gr layers [14, 15]. Also AFM based adhesion force measurements did not yield significant variations with respect to the Gr layer number [54]. However, experimental and theoretical work on the surface energy of graphite [45, 46, 55] yields widely spread values from $\sim 55$-$200$ mJ/m$^2$ which exceed the values specified for Gr $\sim 30$-$50$ mJ/m$^2$ [45, 46]. Therefore, an increase of surface energy with Gr thickness can be expected. Variations in the growth morphology with Gr layer number have also been reported for Au and Ag islands prepared on Gr [16–18]. The varying morphologies of these islands were attributed to decreasing adatom-Gr interaction energies and different diffusion barriers with increasing Gr layer number due to quantum size effects [16]. However, the higher surface energy of graphite should yield a higher wettability of graphite compared to graphene which is obviously not the case for 6P. However, measurements of the interface adhesion energies between Gr and various substrates also showed a significant dependence on the Gr thickness [56]. The strong adhesion for single layer Gr compared to thicker Gr membranes were attributed to the high mechanical flexibility of single layer Gr that allows to deform perfectly with the substrates. Further theoretical investigations indicate that membrane thickness, membrane size, and interface conditions strongly determine the adhesion properties due to the elastic energy stored in the Gr sheet [57]. The wetting of Gr by 6P is apparently much more complex which becomes even more evident when analyzing the arising layer dependent 6P morphologies further.

From the AFM topography images in Figs. 2 a) and 3 a) it is obvious that the difference in morphology is not just restricted to needle length and height but also to the growth direction and the resulting pattern. In Fig. 6, the distributions of needle growth directions and their corresponding length distributions for different Gr layer numbers are presented. The azimuthal needle angle distribution for the SLG (Fig. 6 a)) exhibits four maxima. The angle differences between these maxima yield the relative orientation angles between the 6P needles on SLG. Here, we find angles of $(20\pm7)^\circ$, $(33\pm7)^\circ$, $(60\pm7)^\circ$, and $(82\pm7)^\circ$. Therefore, it is obvious that discrete pref-

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erential orientation angles of the 6P needles exist. Note that the values were obtained by averaging over the peak areas between the minima. Therefore, the given mean values do not necessarily coincide with the peak maxima in the histogram. The corresponding needle length distribution (Fig. 6 b)) shows that needles up to \( \sim 6 \mu m \) length can be found, but \( \sim 85\% \) of the needles are shorter than \( 2 \mu m \) resulting in an average needle length of just \( 1.0\pm0.9 \mu m \). For the angular orientation distribution on SLG II (Fig. 6 c)), just one distinct maximum and a second rather broad one can be found. The resulting relative orientation angles are smeared between 85° and 100°, which indicates a less ordered film. This is also consistent with the optical impression of the film morphology in Fig. 3 a). The according needle length distribution in Fig. 6 d) shows that - similar to SLG - on the SLG-II \( \sim 90\% \) of the needles are shorter than 2 \( \mu m \). The average needle length is \( 1.1\pm0.5 \mu m \) and is thereby a bit larger than on SLG. The reason for this fact is that there exists just a small fraction (\( \sim 8\% \)) of needles smaller than 500 \( \mu m \) on SLG-II whereas on SLG the fraction of needles shorter than 500 \( \mu m \) is \( \sim 20\% \). The angular orientation distribution and corresponding needle length distribution for DLG at 363 K are depicted in Figs. 6 e) and f). Here, a \( \sim 70 \mu m^2 \) area just containing the long needles has been analyzed. The scene is dominated by long needles mainly pointing into two directions with a relative orientation angle of \( \sim 60^\circ \) to each other. On closer inspection, however, it turns out that needles longer than 3 \( \mu m \) just represent a fraction of \( \sim 20\% \). There is a significant fraction of short needles which either grow away from the long needles or are just distributed in between the areas confined by the long needles. In contrast to the SLG, SLG-II, and DLG, the angular orientation of 6P needles grown at 363 K on 4LG (Fig. 6 g)) does not show distinct maxima. However, the distribution can be considered to consist of three rather broad peaks at (33\pm18)°, (89\pm10)° and (145\pm18)° resulting in average relative orientation angles of (56\pm26)°. In addition, the length distribution in Fig. 6 h) shows clearly that the needles are much shorter as in the latter cases. Roughly 95% of the needles are shorter than 1 \( \mu m \).

From a comparison of the layer specific histograms in Fig. 6 and the corresponding specific interface areas in Fig. 5, it is evident that the needles which exhibit the largest specific 6P-Gr interface area also form the most ordered network with well defined needle growth directions. A straightforward interpretation is an increasing 6P-Gr interaction with increasing Gr layer number. However, for a detailed interpretation the strong anisotropy of the 6P molecule and the resulting consequences on binding and diffusion should also be considered.

A weaker interaction with increasing Gr layer number (as suggested by Zhou [16]) seems evident from the experimental observation but is not easy to understand when considering the van-der-Waals character of the interaction between 6P and the Gr. Assuming that the interaction can be well described by the Lennard-Jones (LJ) 12-6 potential, an addition of layers should always lead to an increase in binding energy because the repulsive contribution vanishes at a typical interlayer distance of about 3.35 Å. This is also reflected in the increased surface energy of graphite compared to Gr. However, especially for such strongly anisotropic deposits like organic molecules with a number of additional degrees of freedom also a couple of different adsorption states representing local minima in the potential energy can exist. Moreover, for small molecules finite size effects may also play a role in defining the energetically most favorable adsorption site [58]. As already seen for the 6P/Gr sample at 333 K (Fig. 1 a)), adsorption states can differ significantly in geometry and resulting interface energy and therefore also exhibit different wetting behavior. Moreover, significant kinetic barriers might exist preventing the system from adopting the state with lowest free energy which can result in considerable deviations of the system’s behavior from that expected from energy minimization.

Indeed, Hlawacek et al. [32] calculated different initial adsorption geometries for 6P on SLG and DLG. The most stable configuration on SLG is the 6P long axis aligned parallel to the Gr (0120) direction (favored by \( \sim 0.3 \) eV), whereas for DLG an orientation of the 6P long axis parallel to the (1010) direction is favored (by \( \sim 0.1 \) eV). This shows that additional Gr layers do not only change the total adsorption energy but also alter the adsorption geometry. For increasing 6P coverages, a unit cell similar to the bulk 6P(111) plane was found. Even if 6P aspires the same bulk structure and contact plane for SLG and few layer Gr (graphite) with increasing coverage, the transitions from the different initial situations (long molecular axis || to Gr(0120) or long molecular axis || to (1010)) might follow completely different kinetics due to differences in the involved diffusion paths. This means that - at least at sufficiently low temperatures and moderate time scales - different morphologies can be expected. However, these morphological differences are just kinetically stabilized and will, with time, transform to those structures observed for higher temperatures.

As mentioned above, besides binding energies also diffusion mechanisms play an important role. Especially, in case of processes which are strongly determined by kinetics. For example the formation of 6P needles on Cu(110)2×1-O was shown to be strongly determined by diffusion of 6P molecules parallel to the substrate surface corrugations [27]. For the growth of crystals from anisotropic objects not only the diffusion in terms of transport velocity and direction is important but also the orientation of the molecule with respect to the possible binding position is crucial. The diffusion of organic molecules that are rather large, anisotropic objects with a number of internal degrees of freedom is much more complex than the textbook single atom diffusion. Recently, several publications have been addressed to the diffusion of Gr sheets on Gr substrates [59–61]. These Gr-Gr systems are expected to serve also as model system for the diffusion properties of polycyclic aromatic molecules and other commensurate adsorbate-adsorbent systems [59]. Fast incommensurate diffusion pathways - allowing for molecular rotation - and slow commensurate diffusion, suppressing molecular rotation have been identified [59, 61]. This might play a role in the molecular arrangement processes during growth. However, even though 6P consists of 6 phenyl rings it is not fully commensurate with the Gr, mainly because the single bonds connecting the phenyl rings are slightly longer than the carbon-carbon bonds of the Gr [62]. In addition, finite size
effects might also alter the diffusion properties of the 6P molecules compared to extended Gr sheets [58]. Therefore, a direct comparison of the diffusion properties of 6P with those of fully commensurate, extended systems is difficult. Nevertheless, the concept of fast and slow diffusion paths might still hold. The question whether the activation energies for diffusion vary with the Gr layer number is also not easy to answer. Due to the weak interaction of non adjacent Gr layers, Lebedeva et al. [61] assumed that there is no influence of further layers on the diffusion properties and that Gr should therefore behave in the same way as graphite. Similar arguments were brought forth when investigating the diffusion of noble gases on Gr [63]. There, just a slight variation of the minimum potential energy of the adsorbates with Gr layer number, especially when changing from SLG to DLG, was found. On the other hand, Popov et al. [64] found slight variations in the energy barriers for the relative motion of Gr layers depending on the Gr layer number. Whereas the largest variation was found between 3 layer Gr (1.61 meV/Atom for relative lateral motion, 4.48 meV/Atom for rotation) and 4 layer Gr (1.88 meV/Atom for relative lateral motion, 5.63 meV/Atom for rotation). Reguzzoni et al. [60] calculated an increased lateral potential corrugation upon compression of the Gr layers beyond the equilibrium layer spacing which was attributed to charge transfer from the interlayer region to the near-layer region. Such charge transfer can also appear due to a chemical modification of the Gr interlayer regions or can be substrate induced. A strong influence of the charge carrier density on diffusion was also described by Suarez and co-workers [65]. They investigated theoretically the oxygen diffusivity on Gr as a function of gate voltage. Electron doping increased the oxygen diffusion coefficient on Gr by nine orders of magnitude. This is a quite interesting fact, especially when considering that heating procedures can lead to Gr doping on SiO$_2$ [66, 67] which may significantly alter the diffusion properties depending on the sample history.

Substrate and/or preparational induced local changes in the Gr surface properties can explain the observed morphological changes within one Gr layer (Fig. 1 b), Fig. 2 and Fig. 3). Even though mechanic exfoliation yields the purest form of Gr currently available it is not a too well defined process. The result Gr flakes usually exhibit a wide variation in thickness ranging from SLG to FLG. It is also possible that especially the lowest and the topmost layer exhibit (after transfer) defects originating from the mechanical stress during exfoliation. Also liquids from the transfer process or water from the ambient trapped at the SiO$_2$-Gr interface alter the Gr properties. The heat treatments during deposition can also contribute to changes of the Gr properties, e.g. doping [66, 67], and might therefore also affect the wettability. Additionally, it might happen that adjacent Gr layers are pulled apart during the exfoliation and folded when transferred to the SiO$_2$. An example for a DLG generated by folding is visible on the upper left edge of the SLG-II area in Fig. 3. It seems as SLG-II was initially a part of SLG but has been ripped off during the exfoliation and transfer process. Obviously, the creation of the small DLG edge was not the only change that happened. The whole SLG-II area differs noticeably from the SLG part which is visible in both, the AFM phase and in the 6P morphology. Surprisingly, the specific interface area and boundary length of the 6P structures on SLG-II - even though morphologically different - are still close to those of SLG. It is evident that 6P growth, and therefore the observed morphologies, are very sensitive to subtle changes in the Gr surface properties which vary due to the number of Gr layers but also due to differences at the support-Gr interface or are introduced during substrate preparation. Moreover, the evolution of the 6P films with temperature indicates that the observed structures at lower temperatures are kinetically stabilized and do not represent the global thermodynamic minimum state.

IV. CONCLUSION

The growth morphology of submonolayer para-hexaphenyl thin films, vapor deposited on exfoliated graphene substrates, has been investigated. At a deposition temperature of 363 K, the obtained 6P morphology strongly depends on the number of supporting Gr layers. On single layer Gr, a regular network of straight 6P needles is observed. The needles grow on average shorter and higher with increasing number of Gr layers, thereby

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reducing the specific Gr-6P interface area. Along with this increased dewetting, the network becomes progressively irregular. For a Gr thickness above four layers, no further morphological changes are observed. In contrast, the 6P morphologies observed at lower (333 K) and higher deposition temperatures (393 K) are independent of the Gr layer number. For the lowest deposition temperature investigated (333 K) both, needles and islands coexist on the Gr, whereas for the higher temperatures only needles, forming rather regular networks, are observed. The observed layer dependent dewetting at 363 K cannot be rationalized using classic surface energy arguments. Both, Gr substrate and 6P molecules are highly anisotropic giving raise to discrete 6P needle growth directions. Both, Gr substrate and 6P molecules are highly anisotropic giving rise to discrete 6P needle growth directions. The example of 6P shows that for organics - similar to Au/Ag, however, much more complex - changes in the molecule-substrate interaction come into play and severely impact the film’s wetting behavior. Analog behavior might also be expected for other organic compounds deposited on Gr which has to be considered in organic thin film technology and potential Gr based electronics.

Acknowledgments

This work has been partially supported by the Serbian Ministry of Science through the Project No. OI 171005.

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