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Scalably grown and transferred graphene is a highly promising material for organic electronic applications, but controlled interfacing of graphene thereby remains a key challenge. Here, we study the growth characteristics of the important organic semiconductor molecule para-hexaphenyl (6P) on chemical vapor deposited graphene that has been transferred with polymethylmethacrylate (PMMA) onto oxidized Si wafer supports. A particular focus is on the influence of PMMA residual contamination, which we systematically reduce by H2 annealing prior to 6P deposition. We find that 6P grows in a flat-lying needle-type morphology, surprisingly independent of the level of PMMA residue and of graphene defects. Residual PMMA does however limit the length of the resulting 6P needles by restricting molecular diffusion/attachment. We discuss the implications for organic device fabrication, with particular regard to contamination and defect tolerance. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4913948]

Graphene is a highly promising material for future organic semiconductor device applications due to its unique combination of properties including high carrier mobility, high optical transmittance, chemical inertness, high mechanical strength, and flexibility. Numerous device concepts have been reported, many of which utilize graphene as a transparent, conductive electrode material in contact with organic semiconductor layers. In this context, the growth modes of the organic molecules on the graphene have a key impact on the organics’ (opto-)electronic properties.

While a lot of progress has been made on scalable graphene manufacture, in particular, based on chemical vapor deposition (CVD), controlled transfer and interfacing of graphene remains a key challenge. Graphene layer transfer often involves the use of polymer support, typically polymethylmethacrylate (PMMA), which is challenging to subsequently remove from the graphene. Similar residues arise from lithographic patterning of graphene using resist layers. Technologically relevant, large area CVD graphene is polycrystalline with a range of inherent defects, and upon transfer monolayer or few-layer graphene tends to wrinkle. Despite their potentially crucial impact on organic device performance, the detailed effects of polymer residue, graphene defects, and wrinkles on subsequent organic semiconductor device layer nucleation and growth remain largely unknown.

Here, we investigate the effect of scalable CVD monolayer graphene (MLG) transfer processes (using PMMA) on the growth characteristics of the important, blue-light-emitting organic semiconductor molecule para-hexaphenyl (6P, also called para-sexiphenyl). We find that 6P grows in a flat-lying needle-type morphology on CVD MLG transferred to oxidized Si wafer supports, irrespective of observed PMMA residue levels and MLG defects. This indicates that MLG dominates interface properties even in the case of severe contamination or damage. Preferential 6P nucleation at MLG wrinkles is observed. While residual PMMA does not change the growth morphology of the 6P it severely limits the length of the resulting 6P needles by hindering molecular diffusion/attachment. Only subsequent to post-transfer H2 anneals – that remove even minor PMMA residues – extended 6P needle growth is obtained which resembles that observed on clean exfoliated MLG.

We grow MLG by low-pressure CVD on Cu catalysts. The as-grown MLG on the Cu is then covered with a PMMA layer, and wet chemical etches are used to release the PMMA-coated MLG from the Cu to subsequently transfer the stack onto SiO2 (300 nm) covered Si-wafers. We chose SiO2 as the support due to its widespread use as a model dielectric surface. After transfer, the PMMA layer is initially removed by acetone followed by isopropanol. For selected samples, additional cleaning from PMMA residues is subsequently done by low-pressure (1 mbar) anneals in H2 at temperatures up to 500°C (typical annealing time 3 h). 6P is then deposited onto the transferred CVD MLG via hot wall epitaxy (HWE) with MLG substrates held at 90°C (deposition time 5 min). For further experimental details see the supplementary material.

The small conjugated 6P molecule is chosen as a model system since its growth behavior is highly sensitive to surface conditions, showing two principal growth morphologies (Figure 1): Flat-lying “needle” growth...
(molecular long axis roughly parallel to the substrate surface and normal to the needle’s long axis) is preferred on crystalline substrates whereas upright “island” growth (molecular long axis roughly perpendicular to the substrate surface) prevails on amorphous surfaces including SiO$_2$. Control over these growth morphologies is of key importance for device applications as needle- or island morphologies strongly influence opto-electronic properties of 6P layers. 6P needles characteristically show a high lateral aspect ratio and commonly exhibit heights of tens of nm, as multiple flat-lying 6P layers stack (in herringbone arrangement, see Figure 1) in the needles. In contrast, upright 6P islands form terraced mounds with discrete heights corresponding to multiples of the 6P length of $\sim$2.7 nm. At low coverages usually only mono- or bi-layer islands exist, resulting in comparably small island heights of only $\sim$2.0 nm–5.3 nm (depending on small 6P tilt). This difference in height and morphology makes it straightforward to differentiate needle and island 6P growth based on atomic force microscopy (AFM) (see insets in Figure 1). Previous work on 6P deposition on ultra-high-vacuum-grown and exfoliated MLG demonstrated that for these clean MLG interfaces 6P grows exclusively in the flat-lying needle-type mode under our HWE conditions at 90°C. The flat-lying needle interface is commonly ascribed to strong $\pi$-$\pi$ interactions between 6P’s organic backbone and MLG’s sp$^2$ lattice.

Figure 2 shows a series of AFM topography images of 6P morphologies on PMMA-transferred CVD MLG, starting with as transferred MLG and for samples which were post-transfer cleaned by H$_2$ annealing at increasing temperatures (280°C–500°C) prior to 6P deposition. Only needle-type 6P growth is observed on the CVD MLG, irrespective of H$_2$ annealing treatment. Strikingly, however, with increasing annealing temperature, the needle length increases while the needle areal density reduces. In general, 6P needles nucleate preferentially at the CVD graphene wrinkles and typically extend roughly perpendicular to the wrinkle direction. For the MLG which was H$_2$-treated between 280°C and 350°C, needles also nucleate at lump-like features which we attribute to accumulated PMMA residues (see below). For further increased annealing temperatures of 400°C and 500°C, the longer 6P needles frequently act as nucleation centers themselves yielding the formation of cross or star like needle bunches, similar to 6P deposition on exfoliated MLG.

Figure 3(a) shows a quantitative analysis of 6P needle length distributions as a function of MLG H$_2$ annealing atmosphere. For each histogram, the lengths of 250–500 needles were evaluated. Figure 3(b) shows the average needle length extracted from the histograms. The non-H$_2$-annealed, as-transferred sample exhibits the shortest average needle length, the narrowest distribution, and also the shortest maximum needle length ($<0.5 \mu$m). With increasing annealing temperature, the average needle lengths increase and concurrently the distributions broaden asymmetrically towards larger maximum needle lengths. We note, however, that also the H$_2$ annealed samples continue to feature a significant number of needles shorter than 0.5 μm. For 500°C, where the largest needle lengths are reached, the distribution becomes bimodal: A high number of very short needles ($<150 \mu$m), nucleating at the MLG wrinkles (albeit covering only just over 1% of the surface) can be found in addition to long needles that reach lengths of over 1.5 μm. While we observe an increase in the needle length with H$_2$ annealing temperature, conversely, the 6P needle areal density decreases from $\sim$4.0 μm$^{-2}$ (as transferred) to $\sim$1.5 μm$^{-2}$ (annealed at 500°C after transfer). Typical 6P needle heights and widths range from 20–40 nm to 50–200 nm, respectively.

We concluded that the 6P grows on CVD graphene in a flat-lying needle-like fashion irrespective of the PMMA residue cleaning procedure applied but that the length and density of the resulting 6P needles are strongly dependent on the PMMA removal process prior to 6P deposition. To understand the origin of these dependencies, we investigate the state of the CVD MLG at the point of 6P nucleation. Figure 4(a) shows AFM images of as transferred and H$_2$-annealed CVD MLG before 6P deposition. The non-H$_2$-annealed, as transferred sample exhibits a high density of up to 1 nm high features evenly distributed over the surface, which is ascribed to PMMA residues, in agreement with previous observations on only acetone/isopropanol cleaned substrates.
transferred CVD MLG.\textsuperscript{36} H\textsubscript{2} annealing at 280 °C results in a noticeably reduced surface roughness (root-mean-square, RMS) from 0.8 nm (as transferred) to 0.5 nm (280 °C) in the MLG areas between wrinkles, indicative of the onset of PMMA removal.\textsuperscript{34,36} Further increase of the H\textsubscript{2} treatment temperature successively reduces the surface roughness (down to RMS <0.3 nm for 500 °C), which is attributed to the removal of PMMA residues from the MLG basal planes, with only few isolated larger PMMA residues remaining. Figure 4(b) further quantifies this trend of increasing PMMA removal with increasing H\textsubscript{2} annealing temperature by plotting the relative volume, relative coverage, and average thickness of residual PMMA as function of the H\textsubscript{2} annealing temperature (y-axis partly offset for readability). These quantifications of PMMA residue content were obtained via numerical height threshold analysis on AFM topography data.\textsuperscript{59} (c) Corresponding Raman spectra showing the evolution of the characteristic MLG G and 2D bands and the defect related D band with H\textsubscript{2} annealing temperature. Thus resulting in the observed 6P needle length increase (Figures 2 and 3). For further increased annealing temperatures (350 °C and 500 °C), the PMMA residue reduces in relative volume, relative coverage, and average thickness, in agreement with the visual impression from Figure 4(a) and the RMS roughness decrease to 0.3 nm.

While increasing H\textsubscript{2} treatment temperatures thus result in more efficient PMMA removal, concurrently alterations to the graphene quality occur, as evidenced by Raman spectroscopy.
(Figure 4(c)). The intensity ratio of the 2D/G peaks drops with increasing annealing temperature from ~2.3 (as-transferred) to ~0.7 (500°C), indicative for a change in the graphene doping level and partly consistent with PMMA removal but also with defect formation in MLG.36,38,62 The defect-related D peak starts to rise for 350°C annealing and emerges notably at 500°C. This indicates minor generation of defects up to annealing temperatures of ~350°C and pronounced damage to the MLG for higher annealing temperatures. This means that while high temperature H2 annealing efficiently removes PMMA and thereby enables extended 6P needle growth, it also damages the underlying MLG.

To understand how the PMMA residues influence 6P growth, we compare 6P morphologies on selected reference substrates in Figure 5. 6P is deposited onto (a) exfoliated MLG, (b) spin-coated homogeneous PMMA layers, and (c) filtered-cathodic-vacuum-arc deposited amorphous carbon (a-C) films63 (all on SiO2 covered Si wafers). The exfoliated MLG serves as a clean and defect-free ideal graphene surface, while the PMMA layer and the a-C film represent "dirty" and fully defective graphene, respectively (Raman spectrum of a-C in supplementary Figure S4 (Ref. 59)). We find flat-lying needle growth on the exfoliated MLG (consistent with previous literature12–14) but interestingly a drastic change to upright 6P island growth on both the PMMA layer and the defective a-C.53,54 The 6P island growth on the reference PMMA layer indicates that for extended PMMA residues on MLG, a change to island-type 6P growth would occur. Similarly, the reference a-C result suggests that for high defect levels in MLG a change-over from 6P needle to island growth is to be expected. Equally, in the extreme case when CVD MLG would be so strongly pitted that the bare SiO2 substrate underneath would be exposed, also 6P island growth would be expected as 6P is well known from literature to generally show island-type morphology on bare SiO2.12,60 In Figure 2, however, no upright 6P island-type growth is observed on the CVD MLG irrespective of the PMMA residue and the MLG defect levels revealed in Figure 4. This indicates that the observed PMMA residues on the MLG (even without H2 annealing) do not provide large enough interaction to induce island growth with upright molecule orientation. Thus, 6P growth appears to be still dominated by the π–π interactions between the 6P organic backbone and the sp2 MLG lattice, even for the relatively contaminated MLG. This surprising resilience of the underlying MLG to dominate the interface properties, even in the case of the observed severe contamination, may be a key technological advantage of MLG. Similarly, despite the comparably high defect levels in the Raman data for high temperature H2 annealed MLG (Figure 4(c)), also in this defective MLG the sp2 lattice still appears to dominate as a template to promote 6P needle growth. This highlights the robustness of MLG’s interfacial properties against contamination and defects, albeit future work will be required to understand detailed dependencies on organic molecule species and substrate-MLG interactions.2,13,14,22,29–33

While 6P grows in a needle-type mode on MLG irrespective of PMMA residue and defect levels, the systematic variation of the 6P needle lengths correlates with the amount and distribution of PMMA left on the surface. Only short needles are present on strongly PMMA contaminated samples. In such a scenario, the 6P needles nucleate at graphene wrinkles and extend perpendicular to the wrinkled direction until they terminate at a PMMA contaminated area. This indicates that PMMA limits 6P molecular diffusion and/or attachment.10 This is further corroborated by the comparably high nucleation density just at the wrinkles on the as transferred MLG (Figure 2(a)). Upon H2 annealing, the PMMA is successively removed from the graphene basal plane (Figures 4(a) and 4(b)). The reduction of PMMA residuals results in less influence on 6P diffusion and attachment mechanisms, thus yielding longer needles. As the overall deposited 6P volume is kept constant in our experiments, the larger needle lengths result in the observed lower needle areal densities. In addition to the wrinkles, also the longer needles start to act as nucleation centers for additional 6P needles, and the 6P growth morphology on high temperature H2 annealed CVD MLG approaches the highly crystalline characteristics of 6P needle structures on clean exfoliated graphene.12,13

In summary, we have systematically investigated the effects of transfer-induced PMMA residues and defects on the growth modes of the model organic semiconductor molecule 6P on CVD MLG. 6P grows in a flat-lying needle-type morphology on CVD MLG, irrespective of observed PMMA residue and graphene defect levels. This implies a surprising persistence of MLG in dominating interface properties even in the case of severe contamination or damage. 6P needles nucleate preferentially from wrinkles in the MLG. While PMMA residues do not have an impact on the growth mode of 6P, they severely restrict the length of the resulting 6P needles by limiting molecular diffusion/attachment. H2 annealing prior to
6P deposition however recovers extended 6P needle growth, approaching the characteristics of 6P on clean exfoliated MLG. This underscores the importance of post-transfer cleaning processes for integration of MLG into organic electronics.

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