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Grafold-driven nucleation of pentacene on graphene

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ABSTRACT

Folds in graphene—grafolds are frequently present even after transferring graphene layers, which were fabricated by chemical vapor deposition (CVD), onto SiO₂ substrates. As we are showing in the present Letter, grafolds have a crucial role in determining the morphology of pentacene layers on graphene, and should be as such considered in designing fabrication protocols of pentacene–graphene devices. Our atomic force microscopy investigation of the initial stages of growth of vacuum-evaporated pentacene on CVD graphene shows three-dimensional growth at submonolayer coverages of pentacene. Moreover, islands were found to preferentially nucleate at the location of the grafolds. We interpret this behavior in terms of increased chemical reactivity of grafolds that was predicted in previous theoretical works.

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Graphene's in-plane Young modulus may reach TPa values [1], nevertheless graphene foils can be easily folded in the out-of plane directions. Such folds—grafolds[2] form as strain-relieving features as graphene temperature is lowered after chemical vapor deposition (CVD) of graphene onto copper foils, as described in detail in Ref. [3]. Grafolds are frequently encountered also after transferring of copper-free graphene sheets onto substrates such as SiO₂. In addition to increasing surface roughness of graphene, grafolds alter, locally its chemical reactivity and its electronic structure, and change the total energy of graphene lattice [4]. For graphene-based electronics that is likely to be based on CVD-fabricated graphene, it is therefore important to understand the influence of grafolds on the morphology of subsequent layers on graphene [5]. Graphene-based devices frequently comprise thin layers of organic semiconductors (OSs) that act as primary charge-transporting layer, while graphene is envisioned either as a support or as a charge-injecting layer [6]. One of the most frequently used OSs in organic electronic devices is pentacene—a small-molecule OS that exhibits high charge carrier mobility, and can be readily synthesized in ultrathin layers that exhibit—depending on the layer thickness and growth temperature—one or two polymorphs—thin-film-phase and a bulk-phase [7,8]. On SiO₂, for example, pentacene molecules nucleate in islands whose height does not exceed a length of a single molecule, and that at least two complete monolayers are formed before the third starts to nucleate [9]. Reports of pentacene growth on highly oriented pyrolytic graphite (HOPG) [10] and graphene [11] indicate less ordered growth exhibiting a three-dimensional (3D) morphology.

In this work we have focused on the nucleation phase of growth of pentacene on CVD-grown graphene transferred onto SiO₂ substrates. Special care has been devoted to the preparation of the substrates in order to

remove almost completely the residues of polymethylmethacrylate (PMMA) that is used as a protective cover of graphene during etching of Cu foil, since Lee et al. [11] reported that PMMA islands may act as nucleation sites for pentacene. Our results show, that on graphene surface that has as little as 0.2% of the area covered by PMMA residues, grafolds act as main attractors of pentacene molecules. Also, PMMA molecules are immobile at the substrate temperatures, at which pentacene growth is performed and therefore are less likely to act as nucleation centers. In particular, we found that the sites of intersection of several grafold lines become decorated with pentacene islands that exceed by far the amount of pentacene contained in all other islands. We interpret this phenomenon in terms of enhanced reactivity of graphene at the location of grafolds [12].

The as-received samples of CVD-grown graphene (Graphene Supermarket) comprised 25 μm-thick Cu foil, coated by a single layer graphene on both sides. A 400 nm thick layer of PMMA was drop-cast from a chlorobenzene solution on one of the graphene surfaces at 60 °C. The Cu foil was removed by immersing the samples in iron chloride solution. The 300 nm-thick SiO₂ layer on Si wafer served as a target substrate, and was cleaned in acetone and isopropanol for 10 min each, and subsequently in piranha bath (a mixture of H₂SO₄ and H₂O₂ in 3:1 ratio) for 10 min. The dried PMMA/graphene film was put carefully on a cleaned SiO₂ substrate at 90 °C. To remove PMMA we have adopted the procedure described in details in Ref. [13]. An Atomic Force Microscope (AFM) operating in non-contact mode and recording the topography and the phase signal were used to check the degree of removal of PMMA on representative samples. The pentacene layers were evaporated in a vacuum chamber with a base pressure of 1 × 10⁻⁸ Torr onto the substrates at room temperature. Typical deposition rate was 1 nm/min.

The topography of a pristine graphene surface prior to the deposition of pentacene is presented in a 1 × 1 μm² AFM scan in Fig. 1. The surface is characterized by grafolds whose height ranges from 1 nm

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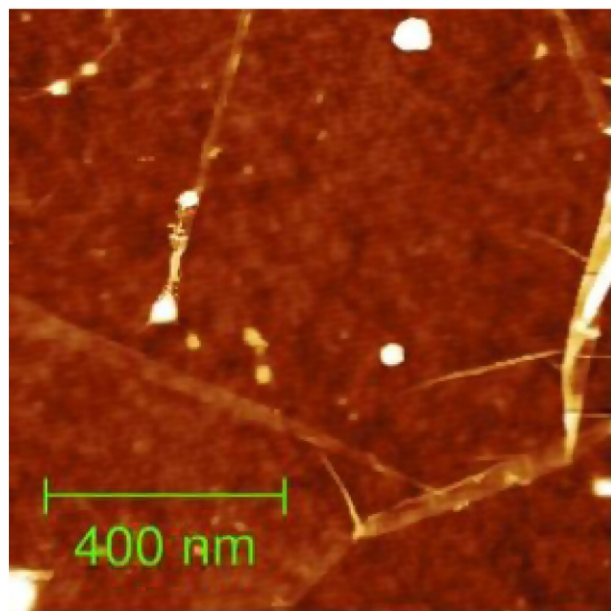


Fig. 1. An AFM height scan of a clean single-layer graphene sheet after transfer onto SiO_2 surface. The size of the scan is $1 \mu\text{m} \times 1 \mu\text{m}$. The straight features are folds in graphene sheet—grafolds. The lowest grafolds are 1 nm high, and the highest are 6 nm high. Upon transfer of graphene onto the substrate the samples were heat-cleaned at 500°C for 1 h to remove most of PMMA. Oval features with typical height of 20 nm are residues of PMMA and represent a coverage of less than 0.2% of the graphene surface.

(single-folded graphene) to 6 nm (multiply-folded graphene). In addition to grafolds we observe residues of PMMA as 20 nm high oval features covering less than 0.2% of the surface. On such surfaces a pentacene layer was deposited and exhibited a morphology in its nucleation phase as demonstrated in Fig. 2, where we show a representative $3 \times 3 \mu\text{m}^2$ AFM height scan of a graphene surface covered by a pentacene layer with a nominal thickness of 0.9 nm. The image shows lines that correspond to grafolds of typical height of about 2 nm. Bright ovals are pentacene islands, and small dots are the PMMA residues. Since the false-color scale was adjusted so that grafolds are visible, the highest islands appear white. The majority of the islands are located near the grafolds, and in particular, at the points of intersection of several grafolds. Also, the islands in these spots are higher than average, and exhibit larger projected area than the islands that nucleate either on the flat areas of a graphene surface or at the straight sections of the grafolds. This is further evidenced in Fig. 2(b), where we show the probability density histogram of island height. We see that, in addition to the leftmost peak corresponding to the lowest islands, an additional peak is observed at around 27 nm, and corresponds to the islands located at the intersections of grafolds. To measure the island height a polynomial background plane subtraction has been performed and zero of the height was set to the resulting background plane. The height of the islands was recorded relative to this reference. However, since graphene layer delamination off the SiO_2 surface may occur this procedure could lead to an overestimation of the island height. Therefore, the height of each island has also been checked, by measuring its height close to the island. In addition, the histogram shows a bimodal distribution that is likely a consequence of two different growth rates. The higher growth rate, resulting in higher islands, could stem from an increased chemical reactivity of the intersection of several grafolds, as discussed below. We see that the growth of pentacene on wrinkled graphene is of Volmer–Weber type. The work of such heterogeneous nucleation of 3D islands is proportional to the supersaturation, i.e. the difference of the chemical potentials of the pentacene vapor and pentacene crystal at a given pressure, and the size of a critical nucleus [14].

Increasing the pentacene coverage to nominally 3 nm, pentacene islands enter into the coalescence phase. As shown in Fig. 3a, the islands

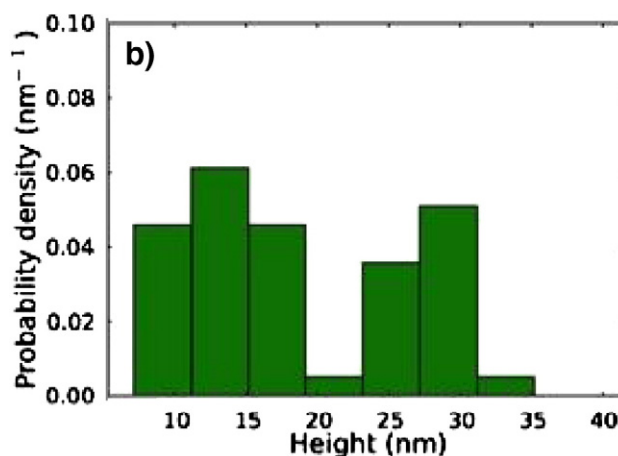
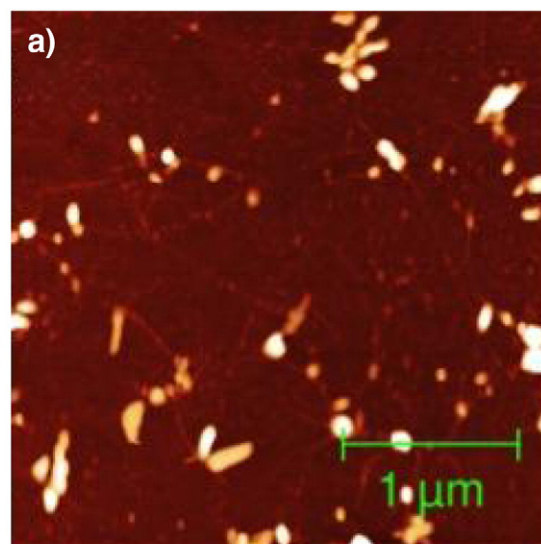


Fig. 2. a) A $3 \times 3 \mu\text{m}^2$ atomic force micrograph of graphene surface covered by nominally 0.9 nm of pentacene at room temperature. Bright tones correspond to higher elevations. Thin lines are grafolds with typical height of 2 nm. Bright oval shapes are pentacene islands with the average height of about 27 nm. The false color scale was intentionally shifted so that the grafolds are apparent. The highest islands therefore appear white. b) A histogram showing the probability density for the island height of panel a. The histogram is the result of data obtained from 75 islands.

continue their elongated morphology already observed in some of the islands in Fig. 2a. They appear as assembled by coalescence of the islands of the type shown in Fig. 2a. Assuming that pentacene molecules attach to the graphene surface with flat face on the surface [10,15] the in-plane lattice mismatch amounts to 0.84 and 0.59 in the c and b directions of the unit cell, respectively. As demonstrated, for example, by Tersoff and Tromp [16] islands undergo a shape-transition phase as their size increases beyond the critical size. In order to compensate the elastic strain resulting from the lattice misfit they adopt a long, thin shape. The islands are also higher at the intersection of grafolds (rightmost peak in Fig. 2b). The island height decreases as the island extends away from the grafold intersection. In Fig. 3b we show the height distribution of the islands. The histogram indicates that with increasing coverage the maximum island height does not increase significantly beyond that observed in the nucleation phase (Fig. 2). The incoming pentacene molecules become attached to the sides of the existing islands that propagate along the grafolds or perpendicular to the grafolds. The maximum attainable height is likely a consequence of the lattice mismatch between the pentacene and graphene unit cells, and the associated strain present in the highest islands [16].

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