The influence of substrate temperature on growth of para-sexiphenyl thin films on Ir{111} supported graphene studied by LEEM

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1. Introduction

In recent years, the growth of organic semiconductors on solid substrates has received significant attention for both scientific and technological reasons. One such organic semiconductor is para-sexiphenyl (6P), a rigid rod-like conjugated molecule. Thin film growth of 6P molecules has been investigated intensely due to the unique optical and electronic properties of the molecule. These properties are found to be subject to substrate anisotropy and also depend on the arrangement of the molecules in a thin film [1,2]. The molecular orientation can be controlled by using appropriate substrates from lying [3] to upright standing [4]. In-depth knowledge of the growth behavior as a function of temperature is a key to controlling the thin film structure and exploiting its full technological potential [5].

In several recent publications it has been shown how the growth parameters can be used to tailor the morphology of 6P thin films on different substrates [6–8]. In this paper, we investigate the growth and structure of 6P molecules at different surface temperatures on epitaxially grown graphene sheets supported by an Ir{111} surface. The layers and needles that form on graphene as well as the ramified structures that grow on Ir{111} are studied as a function of substrate temperature. The role of defects in the graphene sheets is also analyzed using Low Energy Electron Microscopy (LEEM) and Photoemission Electron Microscopy (PEEM). Micro Low Energy Electron Diffraction (μLEED) is used to locally obtain structural information [9].

2. Experimental

The experiments are carried out in an Elmitec LEEM III apparatus of Bauer's design [10] with a base pressure of less than 1 × 10−10 mbar. A 1.4 μm field-limiting aperture has been utilized to collect local structural information from features of interest. An Ir{111} substrate is atomically cleaned by exposing to low pressures of O2 at elevated temperature. Graphene films are then prepared by Chemical Vapor Deposition (CVD) of ethylene (C2H4) on the Ir{111} surface at a temperature of 875 K [11]. The growth of the graphene flakes follows in-situ using PEEM until sufficiently large graphene flakes have formed on the Ir{111} surface. A LEEM image of such a flake is shown in Fig. 1(a). Substrate steps (thin lines, indicated by white arrows) are still visible in Fig. 1(a) as the graphene flake follows the topographic contours of the underlying substrate. A network of straight linear features (indicated by black arrows), appearing much darker and wider than the steps, is also visible on the graphene. These linear features are wrinkles in the graphene sheet that result from elastic relaxations that occur when the sample is cooled from the graphene growth temperature to the 6P deposition temperature. The wrinkles extend about 3 nm from the surface and are a few nanometers in width [12]. Commercially available 6P
3. Results and discussion

3.1. Deposition of 6P at 320 K

A sequence of bright field LEEM images acquired during the deposition of 6P molecules is shown in Fig. 1. Fig. 1(a) shows the pristine graphene surface with graphene wrinkles (thick straight lines) and steps in the underlying Ir[111] surface (thin curved lines). For a detailed discussion of the morphology of graphene flakes on Ir[111] the reader is referred to [11,12,14]. With the deposition of 6P molecules, the intensity of reflected electrons from the graphene decreases, indicating the presence of a diluted phase of 6P molecules on the surface. After 727 s (0.46 6P/nm²) of deposition, nucleation of 6P domains takes place next to the wrinkles. The domains are mobile and move over the graphene surface [15]. After 813 s (0.52 6P/nm²) of deposition, the intensity that is measured on 6P domains reduces even further (indicated by black arrows in Fig. 1(b)). The dark 6P domains grow to form a complete monolayer after 948 s (0.60 6P/nm²) of 6P deposition. For the next 130 s no new features or significant contrast changes are observed. After this, bright 6P crystallites can be observed. These crystallites also nucleate next to the wrinkles, as indicated by the black arrow in Fig. 1(c). In contrast to the initial islands, these crystals are immobile. With continued deposition, they elongate, resulting in a fiber like morphology. Fig. 1(d) shows a LEEM image after stopping 6P growth at 2149 s (1.36 6P/nm²). The graphene surface is covered by a 6P wetting layer of monolayer thickness and long fiber-like structures, which nucleated either from defects in the wetting layer caused by the wrinkles, or from other needles.

Fig. 2(a) shows a µLEED pattern that is obtained from an area without needles which is only covered by the monolayer thick wetting layer. The µLEED pattern consists of the specular reflection surrounded by several rings of LEED spots. It reveals an ordered molecular structure. Within the 1.4 μm aperture that we used to obtain the µLEED pattern several different rotational domains are present. Careful analysis of the µLEED pattern also shows that the 6P molecules are arranged in two different ways, in other words there are two different phases present. The unit cells are highlighted with solid and dotted lines. The length of the unit cell vectors, highlighted with various rotational domains of the ordered 6P structure are visible. (b) µLEED patterns measured from graphene covered with one monolayer of 6P at an electron energy of 14 eV. The specular reflection and other LEED spots associated with various rotational domains of the ordered 6P structure are visible. (b) µLEED pattern measured from a graphene area covered by needles at an electron energy of 21 eV. The LEED spots are marked with red circles to guide the eyes. (c) Molecular arrangement corresponding to the dashed unit cell in (a). The unit cell contains one face-on molecule. (d) Sketch of the molecular arrangement corresponding to the solid unit cell in (a). Two molecules per unit cell in an alternating face-on/edge-on configuration are found here. The molecular arrangement in the needles (b) is similar to this second denser phase present in the wetting layer.
bundles of needles grow away from the wrinkles (Fig. 1(d)). The needles have the same ordering as the underlying substrate does not allow the molecules being nearly identical. The unit cell vectors are: 5.0 Å by 9.1 Å at an angle β of 105° and Θ = 25° (Fig. 2(b)). Considering the above mentioned measurement precision and the fact that some of the molecules would need to be shifted only slightly by fractions of an Ångstrom to reach a well coordinated site. The 6P molecules are arranged in a similar (up-right standing) fashion as in the (100) plane of the 6P bulk crystal.

A typical µLEED pattern taken from needles is shown in Fig. 2(b). It consists of LEED spots from a single domain and thus reveals an ordered molecular structure. The dimensions of the unit cell vectors are 9.5 Å and 26.9 Å at an angle β of 69°. The molecular arrangement is similar to the second denser phase found in the wetting layer (Fig. 2(d)). Again these values are very similar to the size of the 6P Ĭ1��11 plane. The molecules are arranged in up-right standing fashion as in the (100) plane of the 6P bulk crystal.

The growth of 6P on graphene at 320 K can be summarized by the following four steps. (1) An initial layer of only flat lying molecules is formed on the graphene surface. This layer nucleates next to the wrinkles. (2) When a critical coverage is reached, the initial layer transforms into a bulk like layer (Fig. 1(b)). The molecules obtain a flat face-on / edge-on configuration similar to the 6P Ĭ1TT plane. (3) 6P fibers nucleate on top of the monolayer thick wetting layer (Fig. 1(c)). This nucleation occurs next to the wrinkles. (4) Parallel bundles of needles grow away from the wrinkles (Fig. 1(d)). The needles have the same Ĭ1TT orientation as the underlying wetting layer. The azimuthal orientation of the long needle axis is roughly perpendicular to the azimuthal orientation of the long unit cell axis and the long molecular axis.

Nearly all nucleation events are occurring next to the wrinkles. The change in curvature of the graphene next to the wrinkle, strain in the adsorbed 6P islands, and the high mobility are responsible for the preferred nucleation of the wetting layer next to wrinkles and the observed large domain size, which is in the µm range. The preferred nucleation, mobility, and formation of the initial wetting layer of 6P on graphene are discussed in detail elsewhere [13,15]. The wrinkles – by creating a large network of 1D defects in the Ĭ6P wetting layer – are responsible for the preferred nucleation of the needles next to them.

Although the graphene flakes cover extended areas of the Ir[111] surface, they still do not cover the entire surface. The remaining bare Ir[111] surface areas are inspected after stopping the deposition of 6P molecules (1.36 6P/nm²). LEEM images show the presence of irregularly shaped 6P structures, as presented in Fig. 3(a). A µLEED measurement obtained from a branch of one of the irregularly shaped structures is shown in Fig. 3(b). The µLEED pattern reveals that 6P molecules form an ordered structure on the Ir[111] surface. The dimensions of the nearest neighbor cell vectors are 5.0 Å by 5.0 Å at an angle β of 108°. The size of this nearest neighbor cell implies that in these irregularly shaped structures the long axis of the molecules is roughly perpendicular to the surface. However, the cell vectors given above are the nearest neighbor distances and not the real unit cell vectors. This is a consequence of the molecular form factors for the two differently rotated upright standing molecules being nearly identical. The unit cell vectors are: 5.0 Å by 9.1 Å at an angle β of 105° and Θ = 25° (Fig. 3(c)). Considering the above mentioned measurement precision and the fact that some of the molecules would need to be shifted only slightly by fractions of an Ångstrom to reach a well coordinated site. The 6P molecules are arranged in a similar (up-right standing) fashion as in the (100) plane of the 6P bulk crystal.

Fig. 3. (a) LEEM image of irregularly shaped structures of 6P grown on the Ir[111] surface. The Ir[111] surface appears dark and the ramified 6P islands show different shades of grey. (FoV: 15 µm, electron energy: 3.5 eV, deposition temperature: 320 K) (b) µLEED pattern obtained from one of the islands at an electron energy of 194 eV. The nearest neighbor cell is highlighted by red lines. (c) The structural model proposed from the µLEED pattern shown in (b). The molecules are arranged in up-right standing orientation on Ir[111]. Nearest neighbor cell, unit cell and the 5×5 superstructure are indicated by red lines (solid, dashed, and dotted respectively).
Different 6P islands or arms of them can have different azimuthal crystallographic orientations. This has been made visible in Fig. 3(a) by using a slightly off normal incident of the electron beam. As a result different crystallographic orientations show different intensities similar to a dark field image. μLEED patterns recorded away from the irregular structures consist only of Ir[111] spots and a dominant diffuse background. The latter is attributed to an unordered 2D gas phase layer of 6P present on the surface of the Ir.

It is well known that on clean metal surfaces para-n-phenyl oligomers prefer a lying configuration [18–20]. However, small amounts of surfactants will lead to an upright standing configuration of the molecules [19–22]. Therefore, it is reasonable to assume that carbon residues of the graphene growth are causing the appearance of these irregularly shaped structures on Ir[111].

PEEM relies on photo-emitted electrons and therefore depends on changes in the work function of a sample to create image contrast. The clean Ir[111] surface appears dark, since its work function (5.76 eV [23]) is higher than the photon energy (4.9 eV) whereas the graphene (4.8 eV–4.9 eV [24]) flakes appear bright (Fig. 4(a)). However, after deposition of 6P the Ir[111] surface appears brighter than graphene (Fig. 4(b)). The change in contrast is suggestive of a surface work function variation caused by 6P adsorption and the formation of an interface dipole – both on Ir[111] and graphene. The 6P needles grown on graphene (indicated by a red arrow) appear darker than the 6P wetting layer on the graphene (Fig. 4(b)). A white arrow is indicating the irregularly shaped structures on the Ir[111] surface which gives a relatively darker contrast. The 6P covered graphene flakes appear darker than Ir[111] and have lighter shade of grey than the 6P needles. Therefore, the resulting order in brightness (from low to high) of the materials roughly grouped by work function is: Ir[111] and upright standing 6P islands on Ir[111] (both higher or similar to the photon energy), 6P(1T)-needles, 6P(1TT) wetting layer on graphene, disordered 6P on Ir[111]. The non-emitting 6P needles are therefore only visible because they sit on a brighter background. This is similar to the contrast mechanism observed for the case of 6P/Cu(110) 2×1-O [25].

3.2. Measurements at 352 K

Increasing the deposition temperature to 352 K, leads to no principle changes in the film formation process. After the initial two-step formation of a wetting layer – by nucleation of domains near the wrinkles – the growth of parallel needles sets in. Again the needles nucleate either near the wrinkles, or from existing needles creating comb like structures (Fig. 5(a)). As expected, higher deposition temperatures and the resulting enhanced mobility of 6P leads to fewer, but longer needles [26].

A typical μLEED pattern measured from the graphene surface covered by the wetting layer is shown in Fig. 5(b). The μLEED pattern consists of the specular beam reflection surrounded by several rings of LEED spots. This μLEED pattern is similar to the one obtained at 320 K presented in Fig. 2(a). The structure of the wetting layer at this elevated temperature is identical to the one that was already found for the growth at 320 K. Due to the small signal, no reliable structural information could be obtained from the needles. However, taking into account the similarities in the wetting layer and the comparable morphology, one can conclude their structure is similar to the structure at 320 K presented in Fig. 2(d).

Post-deposition (2130 s, 1.35 6P/nm²) LEEM imaging of the Ir[111] surface reveals the presence of branched 6P structures (Fig. 5(c)). All 6P structures on Iridium nucleate at the edges of the graphene flakes. The increased mobility of 6P on Ir[111] at this high temperature requires the stable graphene flakes for nucleation. Once formed, they act as sinks for all 6P diffusing on the Ir[111] surface. A similar structure of upright molecules as observed for the other deposition temperatures is proposed.

A PEEM image acquired after stopping the deposition of 6P is shown in Fig. 5(d). The 6P needles on the graphene flake (indicated with a red arrow) appear darker than the 6P wetting layer in the same way as described above. A white arrow marks the irregular and branched structures on the Ir[111] surface. Again, they show a darker contrast than the surrounding surface. The 6P wetting layer on the graphene flakes itself shows an intermediate grey level.

Post deposition annealing of the film leads to a decay of the structures. From deposition temperature to 381 K 6P structures on graphene and Ir[111] remain intact and immobile (Fig. 6(a)). With a further increase of Fig. 5. (a) t=2130 s, 1.35 6P/nm² 10 μm FoV LEEM image acquired at an electron energy of 2.7 eV and 352 K. A single graphene flake on the Ir[111] surface is imaged after deposition of 6P. The edge of the graphene flake is visible in the upper left part. The graphene flake is covered with 6P needles of different orientation. (b) μLEED pattern measured from graphene covered by the wetting layer at an electron energy of 19.3 eV. (c) 20 μm FoV LEEM images acquired at an electron energy of 2.7 eV and a temperature of 352 K. The Ir[111] surface with an irregular shaped island and three graphene flakes covered with 6P is visible. The 6P island on the Ir[111] surface is connected to the graphene flake. (d) 50 μm FoV PEEM image acquired after stopping the 6P deposition. 6P needles, graphene flakes, and 6P islands on Ir are present and marked by red, green, and white arrows, respectively (352 K).
temperature, first the small and later also the bigger needles start to decay until at 400 K all structures on the flakes have disappeared (Fig. 6(b)). The excess molecules can diffuse off the graphene flake into the 2D gas phase on the supporting Ir{111} substrate. A further increase of temperature results in a shrinking of the – so far unchanged – irregularly shaped structures on the Ir{111} surface. They eventually disappear all at 416 K. When comparing these results to desorption data obtained on other substrates [19,27], uncertainties of the temperature measurements in the LEEM sample holder as well as the low heating rate of only 6 K/min have to be taken into account. The sequence in which 6P desorbs from the different substrates is further evidence underlining the weak interaction of 6P with graphene.

### 3.3. Measurements at 405 K

Fig. 7 is a sequence of images recorded during 6P deposition at 405 K.

Fig. 7(a) shows the initial situation. The reflected intensity from the Ir{111} surface decreases with deposition time, indicating the presence of a diluted phase of 6P on the surface. However, at this elevated temperature neither the formation of a wetting layer, nor the nucleation of any other 6P structure is observed on graphene. We believe, that the already large diffusion length of 6P at lower temperatures (i.e. as low as 240 K [13]), will be of the order of the radius of the graphene flakes (roughly 2 μm) at 405 K. As a result, the 6P molecules diffuse from the flakes onto the Ir{111} surface, where 6P domains nucleate at the edges of the graphene flake. This process begins after 230 s (0.14 6P/nm²) of deposition (Fig. 7(b) and (c)). The contrast enhanced centers of Fig. 7(b, c) allow to distinguish between the graphene flake (left and brightest), ordered 6P film and 6P gas phase (upper right). However, the borders between the different areas (in particular in Fig. 7(b)) are affected by a LEEM image artefact related to abrupt changes in morphology and work function [28].

A μLEED pattern obtained from the dark band next to graphene flake in Fig. 7(c) on the 6P covered Ir{111} surface is shown in Fig. 7(d). Only very diffuse spots can be found, superimposed on a homogeneous, diffuse background. The crystalline quality of this film is not very high. The nearest neighbor cell highlighted in Fig. 7(d) has a size of 5.0 Å by 5.0 Å with an angle β of 120°. The obvious way to accommodate the 6P molecules into such a small space is in an upright standing way where the long molecular axis is roughly perpendicular to the substrate. Using the unit cell of the bulk [100] plane (8.091 Å by 5.568 Å and β = 90° [16]) as a starting point we can deduct the unit cell of 6P on Ir{111} to be 8.7 Å by 5 Å and β and Θ = 90° (dashed line in Fig. 7(e)). Compared to the bulk structure this unit cell is compressed along the short axis. The resulting matrix notation of the overlayer with respect to the underlying Ir{111} is given by the following quasiepitaxial coincidence type II relationship [17] (19 13 19 0). Using the same arguments as for the previous structures a 6×6 superstructure describes the situation more precisely and results in the following matrix notation (11 22 0) which is depicted in Fig. 7(e). The distortion of the 6P unit cell is geometrically justified as the molecular rows will have the substrate dictated 120° angle.

Figs. 6. 6 μm FoV LEEM images acquired at an electron energy of 2.7 eV and temperature of 405 K. (a, t = 0 s) A graphene flake residing on the Ir{111} surface prior to exposure to 6P. Wrinkles and the contours of Ir{111} surface steps are visible on the single layer graphene flake. (b, t = 831 s, 0.53 6P/nm²) The nucleation of a 6P flake, as is witnessed by the appearance of a band of different intensity at the edge of the graphene (see contrast enhanced center). The reflected intensity from the Ir{111} surface decreases. Three different levels of contrast are found. From left to right: graphene, ordered 6P layer and 6P lattice gas on Ir{111}. (c, t = 1391 s, 0.88 6P/nm²) The ordered 6P film extending from the graphene flake has grown further (see contrast enhanced center). (d) A μLEED pattern is measured at electron energy of 25.6 eV using a 1.4 μm field-limiting aperture from the Ir{111} surface area completely covered with the ordered 6P layer. The nearest neighbor cell is highlighted by red lines. (e) The structural model proposed from the μLEED pattern shown in panel (d). The molecules are arranged in an up-right standing orientation on Ir{111}. The unit cell (dashed line) and the nearest neighbor cell (solid line) are shown. The 6×6 superstructure is indicated by a dotted line. Times indicated are measured with respect to the start of 6P deposition.
The 6P needles form after the completion of the wetting layer. This is observed for 6P films formed from flat lying molecules [3]. Defects of the Ir{111} substrate – a result of carbon residues after the growth of ramified structures consisting of upright standing 6P molecules. However, with increasing sample temperature (compare Fig. 1(d) at 320 K to Fig. 5(a) at 352 K), less but longer 6P needles are formed on graphene. In addition 6P nucleation on the Ir{111} surface gets increasingly difficult and ramified islands of upright 6P are exclusively nucleated at the rim of graphene flakes. Further increase of the deposition temperature to 405 K results in a considerable change of growth behavior. Neither a wetting layer, nor any three dimensional needles are observed on graphene. A 6P(100) layer does, however, nucleate at the edges of the graphene flakes. It grows on the Ir{111} surface in a step flow–like fashion. This layer built from upright standing molecules shows poor crystallinity.

Our study illustrates that at all temperatures investigated, the growth behavior of 6P on graphene and Ir{111} is governed by defects. Up to 352 K, graphene wrinkles dictate the nucleation and growth behavior of the 6P wetting layer, and needles. At 405 K, the edges of the graphene flakes are the sites where 6P domains develop on Ir{111}.

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References