



# Study of copper-phthalocyanine and pentacene film growth on transferred graphene: The influence of polymer residues



Bi-Yun Shi, Wei-Dong Dou\*

Physics Department, Shaoxing University, Shaoxing 312000, China

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## ABSTRACT

Wet transferring of chemical vapor deposition (CVD) graphene with the assistance of poly(methyl methacrylate) (PMMA) usually leaves polymer contaminations onto graphene surface. Knowledge about the influence of PMMA residues on organic film growth properties is crucial for graphene-related organic electronic devices. In this study, we investigate growth properties of copper-phthalocyanine (CuPc) and pentacene on PMMA contaminated graphene substrate. Grain size and morphologies of CuPc and pentacene films were found to be governed by the density of PMMA residues on graphene. Nevertheless, the molecular packing structures of CuPc and pentacene respond differently with the density with PMMA residues. CuPc molecules tend to nucleated into grains with molecular  $\pi$ - $\pi$  stacking parallel to graphene surface, which is irrespective of the PMMA residues. Whereas the packing behavior of pentacene on PMMA-transferred CVD graphene is sensitive to the density of PMMA residues. Molecular  $\pi$ - $\pi$  stacking perpendicular to graphene is observed when pentacene was deposited onto as-transferred graphene. Parallel mode was observed only on the substrates without PMMA residues.

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## 1. Introduction

Film morphology and crystallinity of organic film play critical roles in organic devices such as organic photovoltaics (OPV) [1,2], organic field-effect devices (OFET) [3,4], organic sensors and radio frequency identification (RFID) [5,6]. The device performance can be greatly improved by optimizing the crystalline structure and film morphology of organic thin film (OTF) owing to the increment of the charge carriers' mobility. Therefore, the improvement of OTF quality is crucial for specific organic devices. This has triggered vast studies about the growth properties of OTF on various substrates including metals, plastic substrate, indium tin oxides (ITO) and silicon dioxide [7–11].

Graphene has been widely used in various OTF devices as electrode materials due to its excellent properties in electric conductivity, mechanical flexibility and optical transmittance [12–16]. This has triggered vast studies about organic film growth properties on graphene as well as the corresponding interfacial electronic structures. Organic molecules having planar backbones usually adopt lying-down geometry on clean graphene surface, i.e. the molecular plane is parallel to the surface of graphene. This geometry usually leads to perpendicular  $\pi$ - $\pi$  stacking which means that the molecular  $\pi$ - $\pi$  stacking direction is perpendicular to graphene surface. This mode is propitious for OTF devices with vertical device structures such as OPV, whereas it is unfavorable for electronic devices with lateral device structures such as OFET. W. H. Lee et al.

demonstrated that polymer residues remaining on graphene surfaces can induce a stand-up adsorption of pentacene, resulting in molecular  $\pi$ - $\pi$  stacking parallel to graphene surface [17]. This observation brings hope to modify the crystalline structures of organic films on graphene with poly(methyl methacrylate) (PMMA) residue. However, M. Kratzer et al. found that para-hexaphenyl (6P) failed to follow this rule when deposited on graphene substrate having polymer residues [18]. Therefore, more work is needed to examine whether this method works or not for other organic material.

Copper-phthalocyanine (CuPc) and pentacene were frequently used as active semiconducting layers in various OTF devices. Charge and energy transport in organic semiconductors is highly anisotropic and dependent on crystalline ordering. Graphene was frequently used as molecular template to optimize the crystallinity of organic layers. For this purpose, graphene was usually transferred to the targeting substrates such as metals and oxides assisted with wet-transfer method which inevitably leaves polymer residues on graphene template. It was reported that the polymer residue substantially influences the film structure of pentacene [17]. However, the influence of the polymer residue on the CuPc film nature still remains unknown. In this work, we investigate how the polymer residues on graphene surface affect the growth behavior of CuPc films. For comparison, the growth nature of pentacene on polymer contaminated graphene substrate was also studied. Although water and gaseous adsorptions on graphene may also influence the growth behavior of organic film, only the role of polymer residues is concerned in this study. Therefore, the possible influence of water and gaseous pollution on OTF film growth was eliminated by

\* Corresponding author.  
E-mail address: [phyth@usx.edu.cn](mailto:phyth@usx.edu.cn) (W.-D. Dou).

annealing the substrates at high temperatures prior the organic depositions.

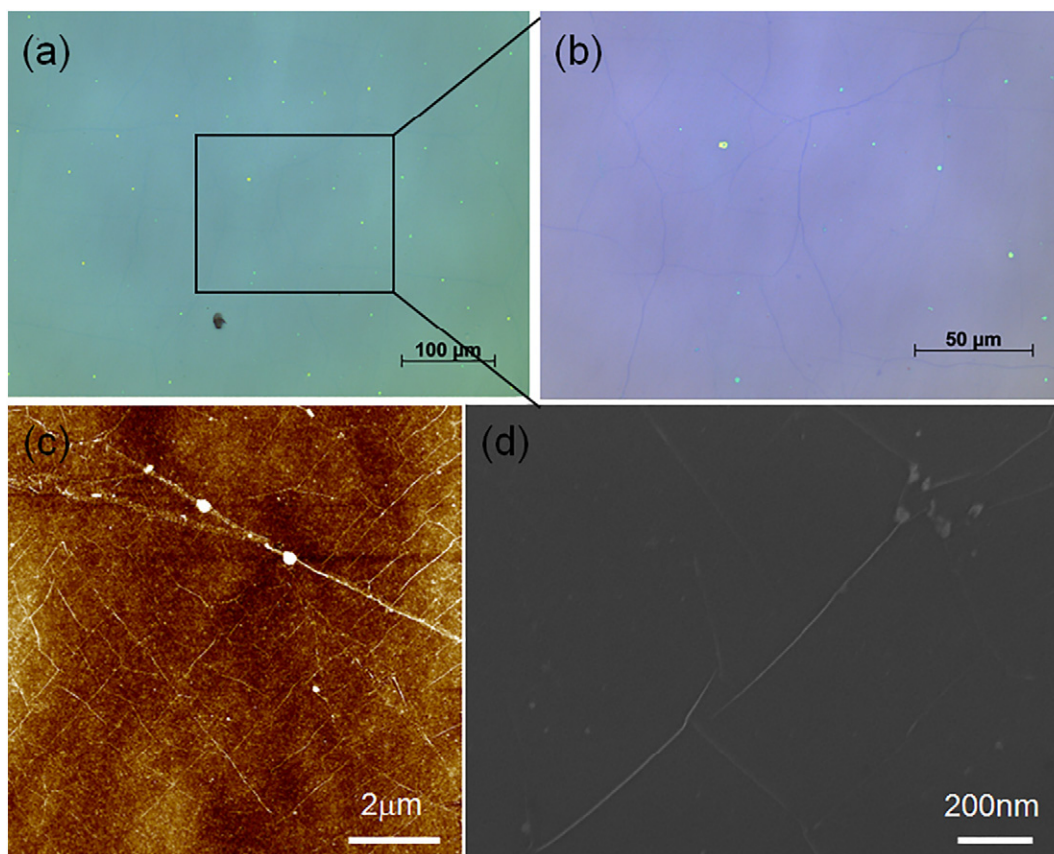
## 2. Experimental details

Single graphene (SLG) was fabricated on copper foils (with a thickness of 25  $\mu\text{m}$ , alpha, 99.96%) using chemical vapor deposition (CVD) which was well documented elsewhere [19]. Then, the graphene samples were transferred onto  $\text{SiO}_2/\text{Si}$  wafers by a polymethyl methacrylate (PMMA)-assisted wet-transfer method [20,21]. Hereafter, the transferred graphene onto  $\text{SiO}_2/\text{Si}$  wafers is called graphene substrate for simplicity. The quality of graphene samples is detected by using optical microscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM) and Raman spectroscopy. Typical optical, AFM and SEM images of the as-transferred graphene are shown in Fig. 1. High quality of SLG samples is verified by the large size of continuous film as shown in the optical images. Wrinkles and PMMA residues can be easily observed on the transferred graphene sample. The removal of PMMA by acetone is generally not attained. This has recently been observed and reported by Paul et al. [22]. We found that PMMA cannot be completely removed no matter how long the PMMA/graphene substrate is immersed in acetone. This observation is consistent with Paul's conclusion. Although PMMA residues may be a drawback of wet-transferred graphene, this method is still employed in this study in order to investigate how the growth manner of organic film is influenced by PMMA residues on graphene substrates. The graphene samples were annealed at various temperatures to remove PMMA before organic deposition. The annealing treatment of graphene and succeeding organic deposition were conducted in a homemade ultra-high vacuum (UHV) system which comprises two UHV chambers, one is for annealing treatment and the other is for organic deposition. The base pressure of both chambers is

better than  $1.3 \times 10^{-5}$  Pa. The graphene substrates were loaded into the annealing chamber and were annealed at various temperatures to partially or completely remove PMMA residues. Hydrogen was fed into the annealing chamber during the heating process and the total pressure in chamber was raised to  $1.3 \times 10^{-4}$  Pa. After that, the annealing chamber was pumped down to the base pressure and the graphene was cooled to room temperature (RT) before it was transferred to deposition chamber for organic deposition without breaking vacuum. Thermal deposition is employed for organic growth. The deposition rate is kept at 0.1  $\text{\AA}/\text{s}$  for each sample. A quartz micro-balance is used to monitor the deposition of organic materials and the thickness of organic thin-film is checked by an ellipsometry measurement. The thickness of both CuPc and pentacene film is set to be 30 nm in this study otherwise declared. The graphene substrates were kept at RT during organic deposition. The morphologies of organic film were investigated using an AFM (Bruker multimode 8) with a tapping-mode. And the crystalline structures of organic films were revealed by X-ray diffraction (XRD) measurements conducted with a Philips X'Pert XRD facility using  $\text{Cu K}\alpha$  emission.

## 3. Results and discussions

Fig. 1 shows the AFM images of as-transferred and  $\text{H}_2$  annealed graphene substrates. High density of particle-like PMMA residues can be clearly observed on the as-transferred graphene (see Fig. 2a). It was reported that PMMA is hard to be thoroughly removed by organic solvent such as acetone [22]. High temperature annealing can effectively remove PMMA contamination and therefore is frequently employed to produce clean graphene samples.  $\text{H}_2$  annealing at 400  $^\circ\text{C}$  results in noticeable reduction of surface roughness due to the removal of particle-like PMMA residues (see Fig. 2b). Fig. 2c and d further convinced



**Fig. 1.** Optical microscopy (a and b), atomic force microscopy (c) and scanning electron microscopy (d) image of as-transferred graphene on  $\text{SiO}_2/\text{Si}$  wafer. Panel (b) is the enlarged image of the rectangular region marked in panel (a). High quality single layer graphene is clearly verified by these images. Wrinkles and particle-like PMMA residues on graphene can be observed in (b), (c) and (d).

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