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Structural analysis of PTCDA monolayers on epitaxial graphene with ultra-high vacuum scanning tunneling microscopy and high-resolution X-ray reflectivity

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ABSTRACT

Epitaxial graphene, grown by thermal decomposition of the SiC (0001) surface, is a promising material for future applications due to its unique and superlative electronic properties. However, the innate chemical passivity of graphene presents challenges for integration with other materials for device applications. Here, we present structural characterization of epitaxial graphene functionalized by the organic semiconductor perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA). A combination of ultra-high vacuum scanning tunneling microscopy (STM) and high-resolution X-ray reflectivity (XRR) is used to extract lateral and vertical structures of 0, 1, and 2 monolayer (ML) PTCDA on epitaxial graphene. Both Fienup-based phase-retrieval algorithms and model-based least-squares analyses of the XRR data are used to extract an electron density profile that is interpreted in terms of a stacking sequence of molecular layers with specific interlayer spacings. Features in the STM and XRR analysis indicate long-range molecular ordering and weak π - π^* interactions binding PTCDA molecules to the graphene surface. The high degree of both lateral and vertical ordering of the self-assembled film demonstrates PTCDA functionalization as a viable route for templating graphene for the growth and deposition of additional materials required for next-generation electronics and sensors.

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1. Introduction

Graphene is a single sheet of sp²-bonded carbon that has tremendous potential for next-generation electronic devices due to its unique physical properties [1–6]. A promising route for achieving graphene-based electronics is the epitaxial growth of graphene on silicon carbide (SiC) (0001) surfaces via thermal decomposition. This process results in graphene formation over wafer-scale areas and enables device fabrication using conventional lithographic techniques [7]. The chemical functionalization of graphene has recently emerged as an important area in graphene research because the integration of graphene in devices and applications requires interfacing graphene with other materials while controlling its band gap and doping [8,9]. Numerous covalent and non-covalent functionalization schemes have been demonstrated on graphene surfaces [8–12]. Recently, interest in self-assembled organic monolayers of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) on graphene has been explored in order to introduce reactive seeding-sites for improved atomic-layer deposition (ALD) of dielectric films [13–16]. PTCDA monolayers exhibit highly ordered growth on a variety of substrates including various metals and reactive surfaces [17–22] and have been extensively studied with a number of techniques including scanning tunneling microscopy (STM) [14,20,23,24], X-ray diffraction (XRD) [24–26], and X-ray standing wave (XSW) [27–30]. In particular, STM probes the lateral structure of PTCDA layers with molecular resolution, while X-ray techniques resolve the vertical structure and allow for characterization of the substrate under the molecular layers. Previous ultra-high vacuum (UHV) STM work has shown that PTCDA forms a well-ordered monolayer on epitaxial graphene on SiC(0001) that is chemically stable and electronically decoupled from the graphene substrate [14].

Herein, we employ a combination of UHV STM and high-resolution X-ray reflectivity (XRR) to characterize PTCDA monolayers on epitaxial graphene on SiC(0001). We derive an atomic-scale structural description of functionalized epitaxial graphene formed on 6H-SiC (0001) substrates through the growth of nominally 1 or 2 monolayer (ML) thick PTCDA thin films, a model of which is shown in Fig. 1. We used high-resolution XRR [31,32] in conjunction with room-temperature UHV STM to obtain the vertical and lateral structure of

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Fig. 1. (A) An idealized depiction of a 1 ML PTCDA/1 ML graphene/6H-SiC(0001) heterostructure with oxygen, silicon, carbon, and hydrogen atoms shown in red, blue, gray, and white, respectively. The crystallographic view corresponds to the [1000] projection of 6H-SiC. The $(6\sqrt{3} \times 6\sqrt{3})$ R30° interface is represented by the closely bonded, dense carbon atomic layer above the Si-terminated SiC bilayer. Nominally, d₀₀₆ = 2.51 Å, d₁ = 2.30 Å, d₂ = 3.35 Å, and d₁ = 3.22 Å. (B) Schematic of the lateral organization of the PTCDA molecules in a herringbone arrangement.

PTCDA layers on epitaxial graphene. We use a combination of Fienupbased phase-retrieval methods [33,34] and model-based leastsquares analyses to derive structures describing the graphene/SiC interface and the PTCDA overlayers. The XRR and STM data show that PTCDA possesses long-range molecular ordering within the surface plane, indicating π - π * interactions between the PTCDA molecules and graphene surface. While previous XRR studies have been conducted on the basic structure of epitaxial graphene and the interface between the SiC lattice and graphene overlayers [35,36], here we use XRR to resolve the interfacial structure of the PTCDA layers on epitaxial graphene on the 6H-SiC(0001) surface. The flexibility of surface X-ray scattering allows it to be applied non-destructively in a variety of sample environments to investigate structures of buried interfaces and/or exposed surfaces.

2. Materials and methods

2.1. Sample preparation

Growth of epitaxial graphene and PTCDA monolayers were performed in a home-built UHV system with base pressures of 5×10^{-11} Torr and separate chambers for sample preparation and



Fig. 2. UHV STM images of the sample surfaces. (A) Clean epitaxial graphene (Sample bias -2.1 V, tunneling current 50 pA, scale bar 20 nm). Inset: atomically resolved image showing the honeycomb lattice of graphene (-0.4 V, 50 pA, 1 nm). (B) Single monolayer coverage of PTCDA on epitaxial graphene (-1.9 V, 22 pA, 10 nm). Inset: Molecularly resolved image showing that the PTCDA monolayer has a herringbone arrangement (-2.0 V, 70 pA, 4 nm). (C) At \sim 1.5 ML PTCDA coverage, the sample concurrently possesses regions with 1 ML and 2 ML PTCDA (-1.9 V, 22 pA, 10 nm). The region to the left of the white dashed line has two layers of PTCDA, while the region to the right has one layer. (D) Schematic depth profiles of the two lines, a–b and c–d, indicated in (C). The SiC step edge in both profiles is the same, but is covered by one layer of PTCDA in line a–b and two layers.

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