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Alignment of benzene thin films on self-assembled monolayers by surface templating

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ABSTRACT

A key question in the epitaxial growth of materials is whether vapor-deposited molecules acquire an ordered structure that depends on the structure and chemical composition of the underlying substrate. In this paper we examine this question for metallic and chemically-tailored self-assembled monolayer (SAM) substrates, and show that proper selection of the templating substrate can lead to the deposition of nearly 100 layer thick molecular films that retain the alignment of the initial interface. In particular, we have examined benzene growth on gold, alkanethiol and phenoxy-terminated SAMs using a combination of in situ infrared spectroscopy and molecular beam techniques. When benzene molecules stick to a clean metal surface, the molecules in the first layer lie flat. However, after the deposition of a few layers, growth occurs as three-dimensional crystallites, resulting in randomly aligned polycrystalline domains. We found that there need not be an orientational transformation from the thin to thick structure for vapor-deposited molecules. Here, we vapor deposited benzene on phenoxy-terminated self-assembled monolayers (SAMs), and grew thick films of aligned benzene molecules. The alignment of the first layer of benzene molecules on the SAM was retained for more than 80 layers. In contrast, when methyl-terminated SAMs were used as a substrate, the thick film structure was indistinguishable from those with Au substrates.

1. Introduction

Organic semiconductors promise significant advantages in both the cost and performance of nanoscale devices over current silicon-based technologies [1]. In order to harness the rich functionality of organic molecules in devices such as light-emitting diodes [2] or field-effect transistors (FETs) [3,4], the interfacial properties between the underlying substrate and the organic materials must be controlled carefully to promote the formation of ordered domains [5,6]. One approach is to employ a well-ordered substrate surface with controlled structure and properties to template the growth of the organic film.

A particular template for the growth of molecular solids is a self-assembled monolayer (SAM) deposited on a metal surface. SAMs made from alkanethiols (R–SH) have found widespread applications in biotechnology, sensors, and surface passivation [7]. The interfacial structures of self-assembled monolayers prepared with normal alkanethiols and derivatives have been investigated for many years [8–11]. The structure of long alkanethiolate monolayers is known to be well ordered with the alkyl chains present in an all-trans conformation and canted off the surface normal by approximately 30°, presenting an ordered arrangement of the terminal groups at the surface [12–14]. What makes alkanethiolate SAMs such a versatile platform is that changing the terminal group of the alkanethiols will create an entirely new surface with its own functionality. Previous studies have shown the importance of the chemical composition of SAM terminal groups on influencing the structure formed by gas-phase deposition on solid surfaces. For example, Laskin and co-workers demonstrated the reactive landing of mass-selected biomolecules via covalent linking to the terminal groups of the SAM matrix, while retaining the secondary structure of the biomolecules [15]. Nakajima and coworkers have successfully used SAMs with different terminal groups to support gas-phase deposited transition metal-benzene sandwich complexes, where the physical integrity of the complexes remained intact, while the orientation and adsorption mechanisms varied by the functionality of the SAM terminal groups [16,17]. However, in these cases, large molecules were used and the delicate interplay between the molecule – molecule and molecule – surface interactions is washed out by the size of the molecules.

Non-covalent interactions between aromatic groups are known to impact a wide variety of phenomena in chemistry and biology [18], and a lot of effort has been dedicated to using aromatic or conjugated materials for the design of materials such as OFETs [19] in supramolecular chemistry [20] and for biological applications [21]. Among the various organic semiconductors investigated thus far, large aromatic polyacenes such as pentacene ($C_{22}H_{14}$) have garnered interest. These materials possess high charge carrier mobility in their crystalline phase and readily form highly ordered polycrystalline films, allowing the fabrication of high-performance thin-film OFET's [22]. Several research groups have

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reported surface-induced growth of ordered layers of these large molecules. On metal or silicon surfaces, pentacene molecules lie flat [23,24]. Often, the terminal groups of the SAM have little effect on the resultant structure of the film [25]. However, a perpendicular orientation relative to the substrate can significantly increase the charge transfer efficiency. Deposition of the desired perpendicular films has recently been obtained by using thiolate SAM buffer layers on Au(111) [26] as well as on Cu(100) [27] surfaces. Alteration of the grain morphology and microstructure of the pentacene film through slight variation of the interactions between pentacene and the SAM caused dramatic differences in OFET performance [28]. Although there are many examples demonstrating the aligning effects of SAMs, the basic physical principles governing organic thin film growth and how these principles relate to the substrate–molecule interactions are not well understood. Results from the study presented here focus on utilizing the fine balance between substrate–molecule interaction and intermolecular interactions to synthesize aligned molecular solids.

In this paper, we present our results for the ordered growth of a model organic precursor, benzene, as a function of the terminal functionalization of the SAM. The experiments were done in vacuum, using molecular beams to expose the surface to the benzene. We show that proper choice of the substrate facilitates the growth of ordered thin organic films. The structure of the terminal groups of the SAMs also has a significant influence on the dynamics of collisions between incoming species and the monolayer surface [29,30]. To demonstrate the strong effect of the substrate, we first characterized the surface structure of the SAMs, and then used a combination of molecular beam techniques to determine the sticking coefficient for benzene incident on a solid benzene surface and Fourier-transform reflection–absorption infrared spectroscopy (FT-IRRAS) to measure the alignment of the component benzene molecules in the organic layer. The growth of benzene films was studied on three different substrates. First, benzene film growth on bare gold surfaces was studied for comparison. The other two surfaces were made from SAMs with two different terminal groups, the first with methyl ($-CH_3$) termination (mSAM) and the second with a phenoxy terminal ($-O-C_6H_5$) group (pSAM), allowing direct comparison as to how the substrate–molecule interactions direct the subsequent growth of the molecular solid.

The IRRAS results clearly discriminate the different degrees of alignment of the benzene overlayers. We show that the benzene overlayer structure varies by substrate and evolves as the film thickens. At lower coverage, benzene in overlayers on pSAMs was highly tilted, while on bare Au, the benzene molecules lies flat. As the coverage was increased, the substrate-induced alignment diminished rapidly on both bare Au and mSAM, but the alignment was retained on pSAM. These results are the first report of such a persistent, and selective, templating of a solid structure in a molecular film from the underlying substrate in a vapor-deposition process.

Supersonic molecular beams provide an ideal tool to control the kinetic energy, incident angle, and exposure in order to influence the kinetics of growth of organic thin films [31]. In this study, we focus on the influence of the substrate surface properties on the adlayer structure, and a low energy beam was chosen. In the range of kinetic energies and incident angles used, no change was detected in the deposited benzene adlayer. In this study, the benzene beam falls into the energy regime where the benzene molecules adopt a combination of orientations with a slight preference in the edge-on mode [32,33]. However, the resulting film orientation was not affected by possible benzene partial alignment in the beam, as confirmed by the generation of the same film structures using either thermal or supersonic beam deposition.

2. Experimental

The experiments were conducted in specially built ultra-high vacuum molecular beam-surface scattering chambers. Previous publications [34,35] have described the apparatus in greater detail, so only a brief overview is presented here. The IRRAS analysis of SAMs and the in situ IRRAS analysis of benzene adlayer growth on different substrates were conducted in an ultra-high vacuum (UHV) chamber with a precision aligned molecular beam source. The sample was mounted on a five-axis manipulator and could be cooled below 120 K with liquid N_2. A PID controller (Eurotherm) controlled the heating of the sample, up to 600 K. A supersonic molecular beam of benzene (Sigma-Aldrich, 99.8%) was generated by bubbling helium or hydrogen through liquid benzene in a room-temperature bubbler, and expanded through a heatable nozzle ($T_n = 300–750$ K) with a 150 μm platinum orifice at a backing pressure of 100 psi.

The beam was characterized using time-of-flight techniques to determine the average energy of benzene in the beam and a liquid N_2 cooled quartz crystal microbalance (QCM) to measure the flux. One monolayer (ML) of benzene on gold is approximately 1.5×10^{14} molecules cm^{-2} [36], and the deposition rate of benzene from the beam on the 110 K QCM was (0.012 ± 0.003) ML s^{-1}. The peak kinetic energy of the beam was varied from 0.40 eV to 1.70 eV by adjusting the expansion temperature and carrier gas. For most experiments, the beam impinged at normal incidence; sticking probability measurements showed a decrease in the sticking probability at glancing incident angles (Θ_i) but no change in the structure of the benzene films on either Au or SAM surfaces were observed at different Θ_i. Benzene was also deposited on Au and SAM surfaces by backfilling the chamber with vapor ($p\approx1\times10^{-7}$ Torr) while the sample was held at 120 K.

The IRRAS spectra were obtained using a Nicolet model 6700 infrared spectrometer with a liquid nitrogen cooled MCT/A detector. The IR light was p-polarized and incident at a glancing angle of 75°. IRRAS spectra of the monolayers and benzene overlayers were collected at a resolution of 2 cm^{-1} and averaged over 500 scans. If not stated otherwise, the IRRAS spectra in this study were collected by the following procedure: (1) cool down of the substrate to the measurement temperature, (2) reference measurement, (3) benzene deposition and (4) sample measurement. The resultant difference spectra thus only show changes in the IR absorption, which includes the peaks due to benzene vibrations and the peaks corresponding to frequency and/or intensity changes of the SAM substrate. Some of the spectra presented have been base line corrected to facilitate the viewing of stacked plots; the corrections are in all cases minor.

Sticking probability (S) measurements were conducted in a separate UHV beam-surface scattering chamber. This apparatus is equipped with a Residual Gas Analyzer (RGA), and the sticking probability was determined using a modified King & Wells method [37] where the RGA signal with the cold surface (115 K) exposed to the beam is subtracted from the signal when the beam scatters from a warm surface where S is nearly zero. This method is well-suited for measuring small changes in S when S is nearly unity, as highlighted in a recent publication [34].

The SAM surfaces were prepared by immersing a cleaned poly-Au on mica substrate (Agilent Technologies Inc.) in a 1 mM solution of the thiol precursor at room temperature for at least 48 h. The SAMs were made from either 11-phenoxy 1-undecanethiol, $SH(CH_2)_{11}OC_6H_5$, (pSAM) or 1-hexadecanethiol, $CH_3(CH_2)_{15}SH$, (mSAM) (Asemblon Inc.). The average thickness of SAMs was measured at five different spots on each sample with a Gaertner L116S ellipsometer ($\lambda = 633$ nm, $n_{SAM} = 1.5$, $n_{Au} = 0.2246–3.5i$). The wettability of the SAM surfaces was determined by static contact angle measurements at ambient conditions. Microliter droplets of DI water were applied at the sample surface by a syringe infusion pump (Harvard Apparatus), and measurements of the contact angle were made on both sides of the two-dimensional projection of the droplet, captured by a video camera with a microscope lens. Each reported angle was averaged over five measurements on the same substrate sample.

3. Results and discussion

The key finding of this study is that phenyl-terminated self-assembled monolayers (p SAM) template the growth of aligned layers