2D Structure of Unsaturated Fatty Acid Amide Mono- and Multilayer on Graphite: Self-Assembly and Thermal Behavior

Naoko Miyashita,[†] Helmuth Möhwald,[†] and Dirk G. Kurth*[,†,‡]

Max Planck Institute of Colloids and Interfaces, Research Campus Golm, 14424 Potsdam, Germany, and National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Japan

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We investigate the self-assembly of oleamide (9-octadecenamide) on graphite by atomic force microscopy (AFM). The molecules, spin-coated from a dilute solution, form a lamellar monolayer due to epitaxial adsorption on the surface. In the monolayer, a small tilt angle boundary is observed indicating a degeneracy in the molecular positioning. The molecular domains preserve their epitaxy to the substrate as the film thickness increases from monolayer to multilayer. Thermal annealing causes changes in the film morphology. Heating the multilayer up to 75 °C results in the formation of large rods, and above 90 °C, large, highly ordered, smooth islands are observed.

Introduction

The preparation of nanostructures on surfaces in a predictable way is one of the key challenges in nanotechnology and nanoscience. Self-assembly, based on weak forces such as electrostatic interactions and hydrogen bonding, provides all advantages of bottom-up procedures over conventional patterning techniques such as self-repair, dimensional control at the molecular level, and parallel fabrication. Understanding the relationship between the molecular structure and the molecular packing in self-assembled films is essential in order to pursue the goal to design functional surfaces at the nanoscale.

The continuous interest in studying fatty acid amides and the amide system in general is based on their abundance and importance, still not fully understood, in nature.[1] Their proven and still undiscovered properties motivate us for further study. In our work, self-assembled oleamide (cis-9-octadecenamide) films of different thicknesses on graphite are prepared and characterized. Direct observation of two-dimensional epitaxial adsorption of monolayer to multilayer is effectively made by tapping-mode AFM.[2] The focus is placed on two parts; the study of the epitaxial adsorption on surfaces, and of the structural changes induced by thermal treatment.

Experimental Section

A dilute solution of oleamide (Sigma-Aldrich, 99%) in chloroform (Fulka) was spin-coated on freshly cleaved highly ordered pyrolytic graphite (HOPG, Plano GmbH) at 40 rps. Multi-mode SPM (Digital Instruments Inc., Santa Barbara, CA) was used in the tapping mode in air with silicon cantilevers (NANO WORLD) with a resonance frequency of 285 kHz and a spring constant of 42 N m^{-1}. Within 15 min after deposition, we observed domain growth. The size and the appearance of the domains stabilized after approximately 30 min. For the thermal treatment, the film was annealed by placing the sample on a hot plate up to 60 min, followed by cooling to room temperature.

Results and Discussion

The AFM image in Figure 1a shows the typical oleamide lamellae on graphite. The height of the lamellae determined by section analysis of the image is approximately 0.2 nm. This value is smaller than the diameter of an alkane chain (approximately 0.5 nm) as determined from the crystal structure analysis. Within the accuracy of AFM height measurement, we conclude that the lamellae have a monolayer thickness. The orientation of the lamellae within different domains shows a 3-fold symmetry demonstrating the epitaxial organization of the molecules along the underlying graphite lattice (see the Supporting Information). We determine the width of the lamella to be 5.2 ± 0.1 nm from the 2D power spectral density (PSD). It is well-known that amides form dimers in solution and in the solid state through hydrogen bonding of the N−H and C═O moieties.[3] Generally, a linear geometry of the hydrogen bond between C═O and N−H with a N···O distance of approximately 0.3 nm is reported from the crystal structures.[4] Considering the length[5] of oleamide in the all-trans conformation of 2.4 nm, the average stripe width corresponds roughly to twice the length of the molecule. Therefore, we conclude that the lamellae consist of H-bonded dimers having a head-to-head configuration with a linear, all-trans conformation of alkyl tails, as shown schematically in Figure 1b. This result is in agreement with STM studies of a related compound, octadecanamide, which report a dimer formation on graphite

* Corresponding author. E-mail: kurth@mpikg.mpg.de.
† Max Planck Institute of Colloids and Interfaces.
‡ National Institute for Materials Science.

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(5) The lengths of the oleamide molecule are 2.37 nm (linear) and 2.13 nm (bent). Calculated from a space-filling molecular model.

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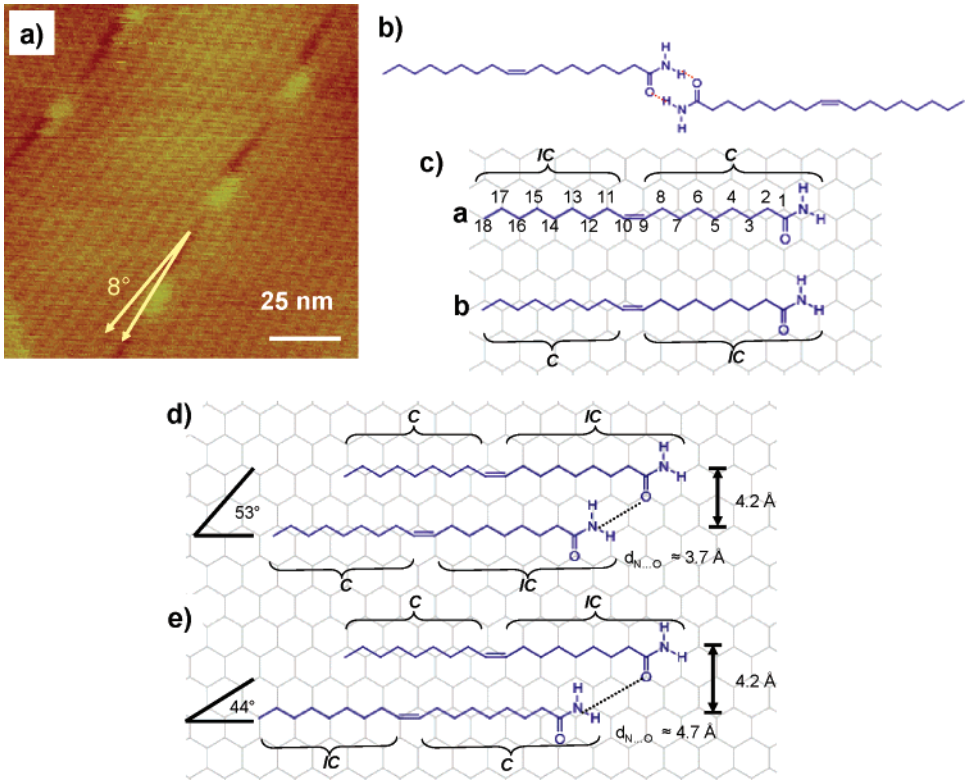

Figure 1. (a) AFM height image of the oleamide monolayer prepared by spin-coating 0.15 mg/mL solution in chloroform on HOPG. (b) Head-to-head arrangement of molecules forming a dimer. Hydrogen bonds are indicated with red dotted lines. (c) Oleamide can adsorb in two degenerate positions on the lattice of graphite which are illustrated in a and b. The two possibilities are illustrated in a and b. The bracket with ***C*** indicates molecular commensurism and ***IC*** incommensurism with the graphite lattice. (d, e) Two different modes of molecular organization of parallel-aligned molecules leading to two different directions at each lamella.

yielding a lamellar periodicity of approximately 4.8−5.0 nm.[6,7]

From the image of a monolayer in Figure 1a, we note that the lamellae are aligned in slightly different directions with respect to each other. Domains with the small-angle grain boundaries are observed at nearby locations with a consistent average tilt angle of 8°. We observe no obvious defects on the substrate in the scanned area where the boundaries are present, so other forces must be operative. A similar observation was reported by Constable et al. and explained by syn and anti conformers of the adsorbate.[8] However, we consider only the linear all-trans conformation because only the extended all-trans oleamide in its dimeric form is in agreement with the lamella width. Dimers with a cis-conformation are too short to explain the experimentally observed lamella width. We, therefore, propose an alternative mechanism based on the degeneracy of the molecular positioning on the surface.

Two types of intermolecular forces, van der Waals interaction from alkyl chains and hydrogen bonding from amide groups, are expected to direct the molecular ordering. As for the adsorbate−substrate interaction, the close lattice match between long alkyl chains and graphite leads to the formation of a 2D crystalline lamellar phase.[9] In addition, the tendency of the protons in the NH_2 group to achieve maximum hydrogen bonding leads to additional secondary interactions between adjacent dimers, resulting in a 2D hydrogen-bonded network on graphite. Presumably, the van der Waals interactions of the alkyl chains with the surface (approximately −7.7 to −8.0 kJ mol^{-1} per CH_2 unit depending on the orientation of the alkyl chain)[10] are stronger than the H-bonding (varies from −57.7 to −53.9 kJ mol^{-1}),[11,12] and therefore determine the molecular ordering. We assume that the planar zigzag carbon skeleton is adsorbed parallel to the surface. In this arrangement, a hydrogen atom of a methylene group closest to the surface occupies the center of a graphite carbon hexagon.[13] What makes oleamide structurally unique, compared to other saturated and unsaturated fatty acid amides, is that it can reach only partial commensurism with the graphite lattice due to the cis-double bond at the midpoint of the molecule. Divided into two parts at the double bond, one-half of the molecule is always found incommensurate. This means that oleamide can adsorb in two degenerate positions on the lattice of graphite as schematically illustrated in Figure 1c. Either the part of the molecule consisting of C1−C9 (a) or of C10−C18 (b) is commensurate with the surface.

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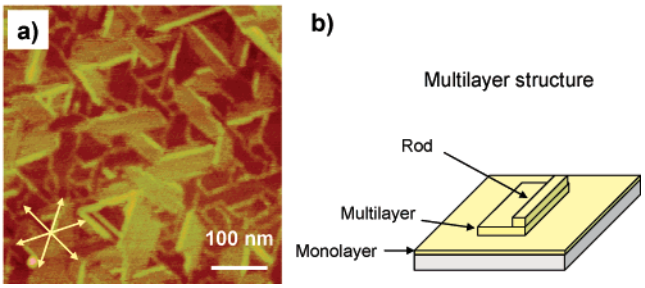

Figure 2. (a) AFM height image of an oleamide multilayer prepared with 0.2 mg/mL solution in chloroform by spin-coating on HOPG. The dark area corresponds to a first layer (monolayer) and bright regions to multilayer islands. Rod-shaped aggregates have dimensions of 40−100 nm in length and 10−13 nm in width. The growth directions of the rods are indicated by the arrows reflecting the symmetry of the underlying substrate. (b) Different regions in the multilayer as observed in (a). The average height of the second layer is 0.6 nm, and the third structure is 0.5 nm.

So far, we have considered only a single oleamide molecule. If a second molecule adsorbs on the surface, it has two choices with respect to the first one depending on which part of the molecule is in registry with the lattice. The alternatives are illustrated in parts d and e of Figure 1. In Figure 1d, both parts of the molecules comprising C10−C18 are commensurate, whereas in Figure 1e, the parts comprising C10−C18 of the first and C1−C9 of the second molecule are. We propose that this degeneracy in the positioning results in domains with small angle differences as shown in Figure 1a. Control experiments with structurally similar molecules support our proposal that a double bond induces degeneracy in molecular positioning on the graphite surface.[14]

We can estimate the small angle difference. The intermolecular spacing of simple alkanes on graphite has been reported to vary from approximately 4.2 to 4.8 Å depending on the preparation conditions.[15] In the simplest case, the molecules assemble along every other lattice axis corresponding to an intermolecular spacing of 4.2 Å. In the vertical direction, the neighboring molecule is shifted by two or two and a half lattice axis. In both cases, the N···O distance of secondary H-bonds remains within a reasonable range (<5 Å).[16] In Figure 1d, the tilt angle is 53° and in Figure 1e, it is 44°, respectively. Therefore, the overall angle difference between domains is 9°. Although this value is in agreement with the experimentally observed small angle difference, we are aware that the organization of the molecules within a lamella may deviate from this simple model and that further detailed investigations are necessary to clarify the details.

Next, we discuss the morphology of oleamide multilayers. The amount of material deposited on the surface is readily adjusted by increasing the concentration of the solution used for spin-coating. Figure 2a shows the AFM image of a multilayer. We can discern three distinct regions. Most prominently, we can recognize rod-shaped aggregates with a length of up to 100 nm and a width of approximately 10−13 nm. Several rods are located at or near the edges of multilayer islands, oriented along directions enclosing angles of multiples of 60 ± 1°. Notably, the rod orientation indicates a long-range interaction through the multilayer. The preferential nucleation of rods along the edges of islands indicates a region of higher surface energy. Figure 2b is a schematic of the multilayer structure observed in the AFM images. We propose that initially the molecules completely wet the substrate forming a monolayer, corresponding to the Frank-van der Merwe mode, the first of three distinguished growth modes[17] observed in our work. Then, as the concentration increases, multilayer islands emerge and continue to grow in size; at the same time, nucleation of rod-shaped aggregates occurs (Stranski−Krastanov growth). Upon further increasing the solution concentration (0.30 mg/mL), we observe the elongation of the rods corresponding to the Vollmer−Weber growth (results not shown, length up to 250 nm and width 13 nm).

Up to this stage, we find that adsorption of molecules results in a multilayer with the presence of rod-shaped aggregates. Now, we study the thermal influence on the film morphology. First, we note that there is no change in chemical composition within the temperature range used for annealing.[18] Compared to the initial AFM images (Figure 2a), the morphology of the multilayer starts to change if the annealing temperature exceeds 75 °C, the bulk melting temperature of oleamide (Figure 3a). The surface is predominantly covered with expanded rod-shaped aggregates. The orientation of the rods begins to deviate from 3-fold symmetry. We observe two average angles now between rods, 61 ± 1° and 68 ± 1°. The angle difference between rods of approximately 8° is similar to the one between lamellae (Figure 1a, vide supra).

Annealing the sample at 90 °C, the surface layer completely reconstructs (Figure 3b). Notably, the short rods grow into long rods that assemble into flat rhomboid islands of various sizes. Most likely, the space between islands is covered by oleamide molecules. The islands have an average height of 0.6 nm. The average angle between rods and islands is close to exclusively approximately 68°. In general, the islands are flat with no or very little texture. However, in some areas, we can clearly see that the islands are highly ordered structures consisting of continuous parallel-aligned stripes (Figure 3b, enlargement in a blue box). From this island, we manually determine the average stripe width to be approximately 8.7 nm. Finally, complete flattening of the multilayered oleamide structure is observed by increasing the annealing temperature to 100 °C (not shown).

Figure 3c shows large, flat, yet highly ordered domains after annealing a monolayer at 90 °C. The continuous stripes found in the domain are in the range of 300−500 nm in

(14) Elaidamide (with a trans-double bond) and stearamide (fully saturated) also show small-angle grain boundaries, though the latter shows a significantly smaller number in the given area. This indicates that the unsaturation of the alkyl chain in the molecule induces the degeneracy in the molecular ordering on the graphite surface.

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(18) TGA in N_2/O_2 shows no evidence of oxidation within the annealing temperature range.

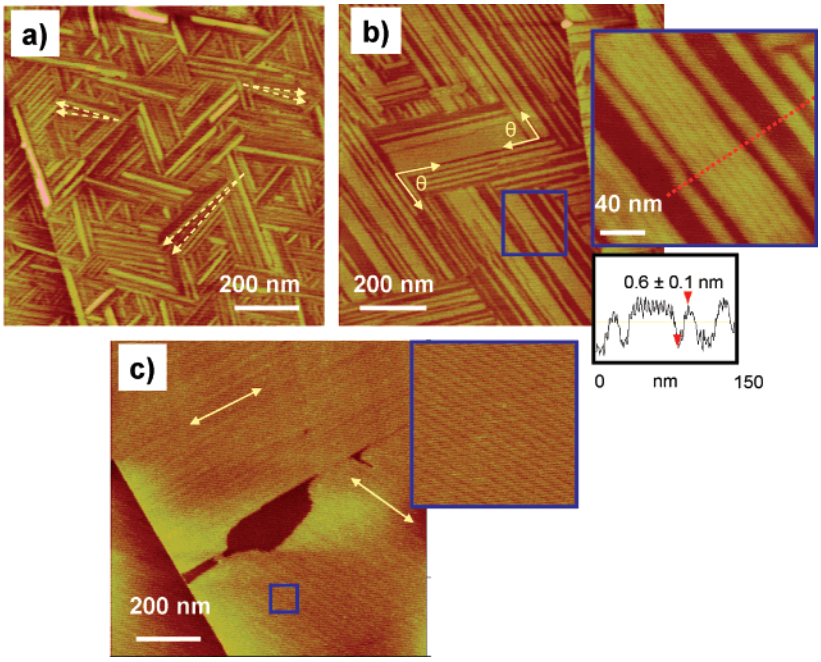

Figure 3. AFM images of oleamide thin films on HOPG after annealing. (a, b) Multilayers prepared by spin-coating a 0.3 mg/mL solution in chloroform. (a) After annealing at 75 °C. The average angle between two dotted arrows is 8°. (b) Annealed at 90 °C. The average angle θ is 68°. The enlarged image of an area marked within the blue line reveals long continuous stripes extending in the same direction with an average stripe width of 8.7 nm. Cross-sectional profile along a red dotted line gives the typical height of the film. (c) AFM image of the monolayer prepared from 0.08 mg/mL solution on HOPG and annealed at 90 °C. Expanded area in a blue box (image size 100 nm × 100 nm) has a stripe periodicity of 5.0 nm. The growth direction of stripes is indicated with arrows.

length, and in some cases larger (≤ 1 μm) before being intercepted by the grain boundary. The stripe periodicity of 5.0 ± 0.1 nm is within the range expected for oleamide. There is a slight decrease in the stripe periodicity before and after annealing (5.2 and 5.0 nm, respectively).

Heating the multilayers provides the energy for the molecules to equilibrate. Most interestingly, annealing of multilayers results in very long, rodlike structures. A similar annealing effect is also observed with alkyl-substituted poly(phenylene) dendrimers on graphite.[19]

Conclusions

This report presents AFM studies of oleamide monolayers and multilayers, and the epitaxial adsorption of self-assembled thin films on surfaces. At monolayer coverage, we observe a small angle tilt boundary between lamella domains. We propose that the double bond introduces degeneracy in the positioning of oleamide molecules on the graphite lattice. One part of the molecule is in registry with the underlying surface while the other part is not. In our view, this is an interesting finding because it offers a route to design molecular layers with structures other than those dictated by the substrate lattice. The multilayer consists of three distinct regions: a monolayer, which covers the surface, islands, and rods, which are often located at the edges of the underlying islands. These high-energy edges may prove useful in nanofabrication. The occurrence of a 3-fold symmetry in the rod orientation indicates a long-range interaction with the substrate lattice. Finally, annealing the multilayer changes the film morphology. At 75 °C, the multilayer reconstructs into rod-shaped aggregates. Heating up to at 90 °C results in large, flat, highly anisometric islands. In the case of monolayer coverage, large, flat islands are formed upon annealing. Such highly ordered, extremely flat, homogeneous films are ideal as molecular templates.[20]

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Note Added after ASAP Publication: The range of the N···O distance of secondary H-bonds was incorrectly reported in the version published ASAP July 25, 2007. The corrected version was published ASAP July 27, 2007.

Supporting Information Available: The additional AFM height image of the oleamide monolayer on HOPG (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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