

Self-assembled alkane monolayers on MoSe₂ and MoS₂

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Highly ordered monolayers of a long-chain molecule, dotriacontane (C₃₂H₆₆), have been obtained by self-assembly at the interface between an organic solution and the basal planes of two semiconductors, MoSe₂ and MoS₂. Scanning tunneling microscopy *in situ* at the solid–fluid interfaces revealed that the adsorbate lattices are close packed and oriented relative to the substrate lattices, but that they are not simply commensurate. The results indicate that for flexible chain molecules, which interact only weakly with the surface of a solid substrate, a high degree of order in the adsorbed monolayers is induced by the atomical flatness of the substrate, while the coincidence of lattice parameters and the specific surface chemistry play only a minor role. Details of the packing, including the symmetry of the adsorbate unit cell, depend on the particular substrate. The results imply that atomical flatness is a key factor for the fabrication of highly ordered organic/inorganic heterostructures.

Highly ordered molecular monolayers on solid substrates are of considerable interest, e.g., for tailoring the surface and interfacial properties of semiconductors. For instance, solar cells may be made from heterostructures based on group VI transition-metal dichalcogenides.¹ A simple and versatile method to prepare compact monomolecular layers on solid substrates is adsorption from solution. In the case of relatively weak adsorption (“physisorption”) it is still an open question which role lattice parameters, surface chemistry, and defects play for the formation of highly ordered adsorbed monolayers. We report here on a model case, i.e., highly ordered monolayers of a flexible chain molecule, dotriacontane (C₃₂H₆₆), on atomically flat terraces of two layered semiconductors, MoSe₂ and MoS₂.

Long-chain alkanes are known to adsorb particularly strongly to the basal plane of graphite. This has led to the conclusion that this system may be a unique case because of the similarity between carbon-carbon bond lengths in alkanes and graphite.² On the other hand, based on thermodynamic adsorption studies it has been argued that the adsorption is driven by a two-dimensional crystallization irrespective of the substrate lattice.^{3,4} Recently, scanning tunneling microscopy (STM) performed *in situ* at the interface between highly oriented pyrolytic graphite (HOPG) and organic alkane solutions has elucidated the structure in considerable detail.^{5–9} It was shown that the small difference in carbon-carbon bond lengths along an alkane molecule and within the basal plane of graphite does persist in the adsorbed monolayer, resulting in an incommensurability of the two linear carbon chains.⁶ On the other hand, the molecular packing within the monolayer leads to a two-dimensional adsorbate lattice, which is commensurate with the substrate.^{5–7} Further STM studies

of a variety of long-chain alkyl derivatives showed that, more generally, the two-dimensional lattice of long-chain alkyl derivatives is simply commensurate with the graphite lattice only in one direction.^{6,9} This implies, however, that the substrate lattice constant does not matter much for the formation of an ordered adsorbate layer. As a consequence, one may expect that closed packed crystalline alkane monolayers could also be formed on other atomically flat and rather inert solid surfaces besides graphite.

An interesting class of layered semiconductors are the transition-metal dichalcogenides, including MoSe₂ and MoS₂. These substrates exhibit lattice constants, which are completely different from the lattice constants of graphite, as well as of a compact alkane monolayer. Moreover, the atomic species at the surface are different. All materials can be cleaved easily to exhibit atomically flat terraces. MoS₂ has been imaged by STM before.^{10,11} Recently, its interface with thin (though not molecularly thin) crystalline films of a series of alkylated cyanobiphenyls was investigated.^{12,13} The results were commonly attributed to adsorbate lattices, which are always simply commensurate with the substrate (even though the different authors suggest considerably different lattice parameters). Monolayers adsorbed to MoS₂ from solution have not been observed yet. MoSe₂ has been studied as a thin film, using STM with a resolution on the nanometer scale.¹⁴ However, atomic scale resolution images of single crystalline surfaces were not reported, nor has any molecular adsorption been observed by STM.

MoSe₂ and MoS₂ single crystals were kindly donated by F. Lévy, Lausanne. Dotriacontane (C₃₂H₆₆, Aldrich) was dissolved in 1-phenyloctane (Aldrich) and applied to the freshly cleaved substrates. The concentration of the solution was varied between 3.6 and 6.7 mg/ml. The STM has been described elsewhere.¹⁵ Tunneling tips were electrochemically etched (2-N-NaOH, 12 V ac) from tungsten wire. All images were recorded in the variable current mode with an average tunneling current of about 2 nA. The tip bias was chosen according to the doping level of the particular sample.¹⁶ It is noted for each image in the

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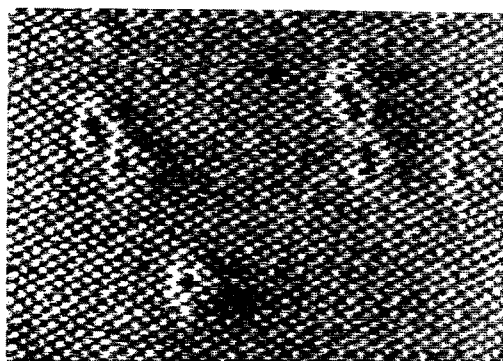


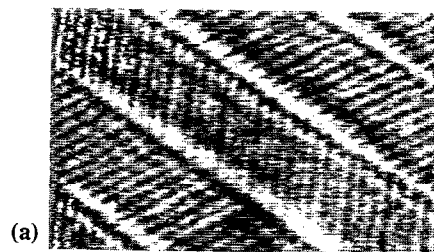
FIG. 1. STM image of the basal plane MoSe₂. $V_t = +0.7$ V.

figure captions. All images are raw data without any image processing.

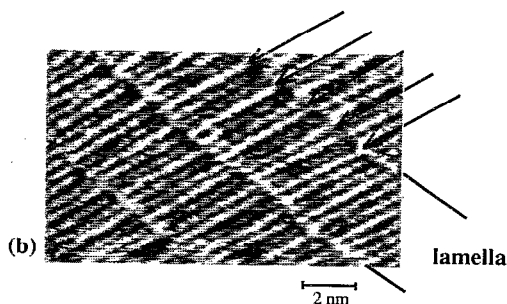
Figure 1 displays an atomically resolved STM image of the basal plane of a MoSe₂ single crystal. The image reflects the threefold symmetry within the basal plane of MoSe₂, similar to the case of MoS₂ (Ref. 11) or HOPG.¹⁷ However, the lattice constants are considerably different in these three cases, namely, 3.29, 3.16, and 2.46 Å for MoSe₂, MoS₂, and HOPG, respectively.¹⁸ Also the surface chemistry is different with selenium, sulphur, and carbon layers at the surface. The width of atomically flat MoSe₂ terraces can be on the micrometer scale with some defects like the single atom defects shown in Fig. 1. The latter have been commonly observed on our samples, and may be attributed to other transition metal atoms substituting Mo.¹⁶

Figure 2 displays STM images obtained at the interface between MoSe₂ and a solution of dotriacontane. The images show highly ordered molecular lamellae of extended molecules, whose long molecular axes are tilted about 30° relatively to the lamellae normal. The tilt angle alternates often (though not regularly) from lamella to lamella between +30° and -30°, resulting in both regions with herringbone structures [Fig. 2(a)] and regions with uniformly tilted molecules [Fig. 2(b)]. Upon lowering the bias towards $V_t = -0.1$ V the image becomes more and more dominated by the underlying substrate structure. Using this effect, it was found that in the ordered monolayer the long molecular axes are always oriented parallel to a substrate lattice axis. Similarly to the case of didodecylbenzene on HOPG,^{19,20} the molecular axes are not oriented at a fixed angle relative to the direction of step edges of the substrate, indicating that the orientation is already induced by the perfectly flat substrate and does not require particular surface defects, as it may be conjectured.²¹

Images, which are determined by both the substrate and the adsorbate simultaneously, may be employed to accurately determine the commensurability between the two lattices. Like in the case of alkyl derivatives on HOPG,^{6,9} it was found that the accuracy required to determine small incommensurabilities could not be achieved by piercing through the monolayer and imaging the two lattices subsequently.¹³ The reason is that the later method requires very precise measurement of absolute distances, which is difficult in general, but is particularly difficult for mono-



(a)



(b)

FIG. 2. STM images of a dotriacontane monolayer on MoSe₂. (a) $V_t = -1.3$ V. The herringbone structure under imaging conditions, where each molecule exhibits equal contrast, implying that the contribution of the substrate to the contrast is very small. The variation of the contrast towards the end of a given molecule may be due to increased molecular dynamics of the chain ends (Ref. 7). (b) $V_t = -0.8$ V. Lamellae with uniformly oriented molecules. Upon close inspection, a modulation of the contrast along the lamellae is revealed, which is not simply commensurate with the molecular lattice. Its periodicity is less than three molecular diameters, as indicated for one lamella by the equidistance arrows.

layers, since here the apparent distances may be influenced by the different frictional forces on the different surfaces. It is suggested, therefore, to carefully examine the experimental basis for claims of commensurability in the literature.

Figure 2(a) shows that under the tunneling conditions employed here, each molecule exhibits about equal contrast, while for a somewhat less negative bias [Fig. 2(b)] some superstructure along the lamellae is observed. Using the usual calibration from the substrate image obtained before applying the organic solution, an intermolecular distance of 4.8 ± 0.2 Å is derived, indicating that the adsorbate lattice constant does not simply scale with the substrate lattice constant. Within the error this value would be consistent with an adsorbate lattice, in which an adsorbate unit cell with three molecules would coincide with a substrate unit cell with five atoms in this direction. However, by examining the superstructures in Fig. 2(b) carefully one has a more accurate method to determine the intermolecular distances relative to the interatomic distances within the substrate. Interestingly, one finds that its periodicity is not exactly 3 but at least 11, indicating a rather high order commensurability, which within the error cannot be distinguished from incommensurability. However, assuming that 11 intermolecular distances d shall agree with a multiple n of the corresponding substrate lattice constant 3.29 Å $\sin 60^\circ$, one finds a more precise value of $d = 4.66$ Å with $n = 18$. This intermolecular distance indicates close packing of alkyl chains with their carbon skeleton plane parallel to the substrate, as found for fatty acids and didodecylben-

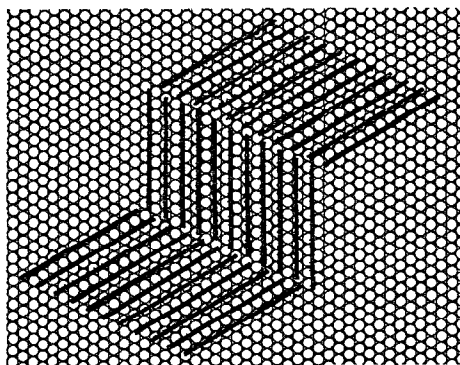


FIG. 3. Model of dotriacontane herringbone structure on MoSe_2 .

zene, but not for alkanes on HOPG.^{6,20} Figure 3 displays a molecular model of a herringbone region. Similarly ordered monolayers have been observed at the interface between a solution of dotriacontane and MoS_2 , the details of which will be published elsewhere.

The results reported above show that close packed and highly ordered monolayers of a flexible long-chain molecule do not only self-assemble at the interface with HOPG, but also at the interface with two solid substrates. While all three substrates are very different as far as lattice parameters and the exposed surface atoms species are concerned, they have in common that they are atomically flat. It is suggested, therefore, that already the flatness of the solid surface induces the order, provided there is some attractive interaction between adsorbate and substrate. This can be readily understood, since the extended and ordered molecular chains maximize the contact area with the substrate surface. Accordingly, the ordered monolayers are always very close packed, contrary to what has been suggested for cyanobiphenyls on MoS_2 .¹³

The details of the packing depend, however, on the particular substrate, since they are determined by very small differences in the free energy, similar to the small differences in the free energies between various crystal modifications in three dimensions. The closest packing is observed on HOPG, which requires the carbon skeleton planes to be oriented perpendicular to the substrate surface,^{6,7} while on MoSe_2 and MoS_2 the skeleton planes are

oriented parallel to the surface, resulting in a 10% less dense packing. The reason for these subtle differences may be that the denser packing is driven by the possibility to gain commensurability on HOPG, which cannot be achieved without losing close packing on the other two substrates with their much larger lattice constants. Molecular modeling studies are under way to elucidate this issue further. A more detailed analysis is also required in order to determine why on MoSe_2 the long molecular axes are tilted relative to the lamella normal by $\pm 30^\circ$, while on HOPG they are parallel to the lamella normal.

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