Direct Observation of Molecular Structure and Dynamics at the Interface between a Solid Wall and an Organic Solution by Scanning Tunneling Microscopy

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(Received 30 November 1990)

A molecular monolayer adsorbed at the interface between the basal plane of graphite and an organic solution of didodecylbenzene has been observed *in situ* by scanning tunneling microscopy at a resolution of 0.2 nm. The monolayer forms a 2D polycrystal with crystallite sizes in the range of a few nanometers. The predominant domain boundary is described by a glide plane. Fast image recording allowed, for the first time, direct observation of the molecular dynamics on the time scale of 100 ms. In particular, the motion of domain boundaries could be associated with diffusing "free volume."

PACS numbers: 68.45.—v, 61.16.Di, 68.55.Jk

The molecular structure at the interface between a solid wall and a molecular liquid is driven by forces which are important, e.g., for a better understanding of lubrication and adhesion, the orientation of liquid crystals through surfaces, or molecular recognition phenomena at interfaces.[1] The order in a molecular monolayer is also a matter of theoretical interest, since true crystalline order cannot exist at any finite temperature in two dimensions.[2] Experimentally, new 2D phenomena have been found for rare-gas adsorbates by synchrotron x-ray scattering[3,4] or for small molecules like nitrogen, ethane, or hexane by neutron scattering,[5] all adsorbed from the gas phase onto graphite. Also low-energy electron diffraction has been employed, e.g., to the hexane layer.[6] However, in the latter case radiation damage or organic molecules is a serious limitation. Much less is known for organic adsorbate layers at the solid-fluid interface. Part of the reason is the experimental difficulty in determining directly the structure *in situ,* since only a few surface-sensitive methods give atomic-scale information about the internal interface between two condensed phases.

Scanning tunneling microscopy (STM) is particularly suitable for the structure determination of monolayers, provided the monolayer is sufficiently immobilized and also contributes enough to the contrast in STM. An important advantage of STM over other high-resolution electron-based surface-science tools is the fact that (1) it is a true local probe able to investigate, e.g., only partly ordered or nanocrystalline structures, and (2) it can be operated both under ultrahigh-vacuum conditions and in various fluid ambients, thereby allowing also the study of the internal interface between a conducting solid and a fluid. One of the first molecular layers investigated by STM was a coadsorbate of benzene and carbon monoxide on Rh(111), prepared under ultrahigh-vacuum conditions.[7] Previous demonstrations of molecular imaging at the solid-fluid interface were on the liquid crystal *n*-octylcyanobiphenyl[8,9] as well as on a solution of the alkane dotriacontane on highly oriented pyrolytic graphite (HOPG),[10] which both exhibit a highly ordered interfacial phase. However, so far neither packing defects nor the dynamics in the monolayers could be observed and analyzed on the molecular scale. In the present study we demonstrate that at the solid-fluid interface STM gives very local information which is suitable not only to determine the packing within a highly ordered phase, but also (1) to determine the molecular structure of defects and (2) to observe molecularly defined dynamics in the monolayer, provided it is on the time scale of milliseconds or longer.

The STM was homebuilt and has been described before.[11] In order to be able to observe molecular dynamics an emphasis was on fast (1 ms per line) and continuous image recording (video tape, real time to the eye). All images presented were obtained at quasiconstant height in the variable-current mode, using Pt/Ir tips. The average current was set to 2 nA and the tip bias was between +1.2 and +1.5 V. *In situ* STM imaging was performed at room temperature at the internal interface between HOPG and concentrated but not saturated solutions of didodecylbenzene [$H_{25}C_{12}(C_6H_4)C_{12}H_{25}$, concentration 10 mg/ml] or dotriacontane ($C_{32}H_{66}$, concentration 2 mg/ml) in phenyloctane, as described elsewhere.[12] The adsorption isotherms of both long-chain alkanes and alkylbenzenes indicate single monolayer adsorption with the major molecular axis parallel to the surface,[13,14] which means that the thickness of the molecular film does not exceed the common tunneling gap width of the order of 0.5 nm.

Figure 1 shows a STM image obtained at the interface between HOPG and a solution of didodecylbenzene [DDB, Fig. 2(a)]. It exhibits two domains, separated by a molecularly sharp boundary. Within the domains lamellae with equal width are observed. The contrast at the position of the benzenes is dominant, but the alkyl side chains are also resolved. At the domain boundary the lamellae are displaced and their orientation is rotated with the plane by 60°. This type of domain boundary is typical for the monolayer. It is so abundant that hardly

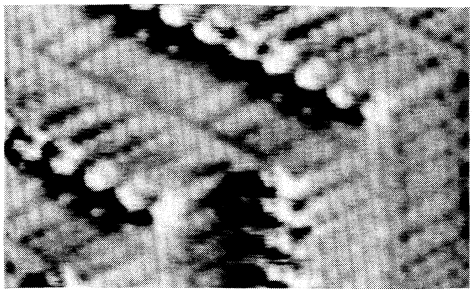

FIG. 1. STM image of a domain boundary in a monolayer of didodecylbenzene adsorbed at the interface between an organic solution and the basal plane of graphite. The strongest contrast results from the phenyl stacks. Evidently the side chains are tilted relative to the lamella boundary and parallel to each other in the adjacent domains. Image size: 7.2 nm ×4.7 nm.

any lamella is longer than about thirty molecules. Figure 2 shows the molecular model explaining the observed images: The DDB molecules are extended, exhibiting their lowest-energy conformation, and lie flat on the HOPG. They pack in lamellae with the long axis of the alkyl side chains forming an angle of 60° with the lamella boundary. The domain boundary is a consequence of the symmetry of the molecule. As a result of the displacement between the two alkyl side chains at the benzene position, a rotation along the long axis of an alkyl chain leads to a symmetrically inequivalent orientation of the molecule relative to the substrate. Two adjacent domains consist of lamellae with the molecules in identical conformations but in the two different orientations. The sharp domain boundary between them is a screw axis. Figure 2 shows that with this particular packing no major holes occur at the domain boundary. Therefore, the energy associated with this defect is small and it becomes understandable why these domain boundaries are so abundant.

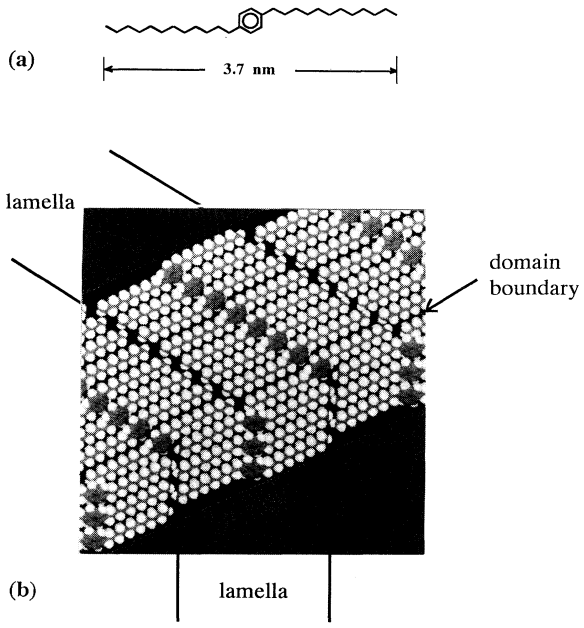

FIG. 2. (a) Didodecylbenzene. (b) Molecular model for the domain boundary of Fig. 1.

The motion of such a domain boundary should to a first approximation cost no net energy. It only requires sufficient thermal energy to allow the cooperative motion

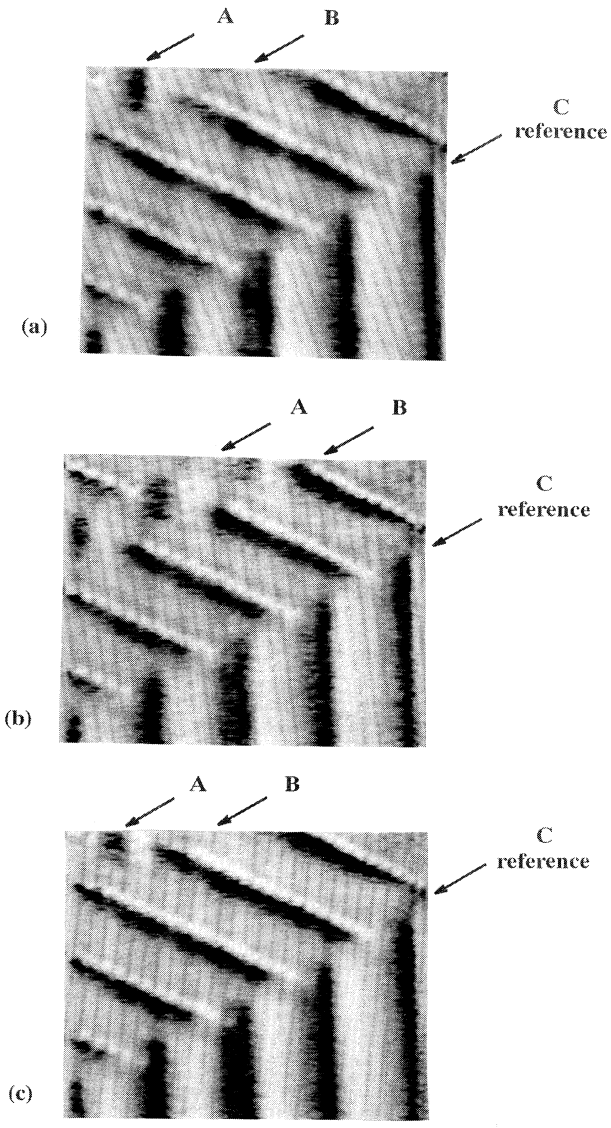

FIG. 3. Motion of domain boundaries, illustrated by snapshots (a)–(c) of a video tape recording the STM images in "real time" to the eye. While the lower domain boundary (*C*) remains fixed in time, the upper ones (*A* and *B*) move first inward [(a)→(b)] and then outward again [(b)→(c)]. The time between the frames, i.e., the lifetime of each configuration, is on the order of 10 s. Image size: 14.5 nm×12.0 nm.

of the molecules involved. The net molecular motion involves the rotation around the long molecular axis and the lateral displacement of the molecule by half the molecular length. The image series Figs. 3(a)–3(c) documents the direct observation of such a process by STM. While the lower domain boundary, *C*, in Fig. 3(a) remains fixed in space for minutes, the upper domain boundaries, *A* and *B*, move inward, 3(b), and outward again, 3(c), on the time scale of a few seconds. The lamellae between *B* and *C* first shrink by four molecules and then expand again. Since at least three lamellae were involved this means that at least twelve molecules had to move cooperatively in this domain.

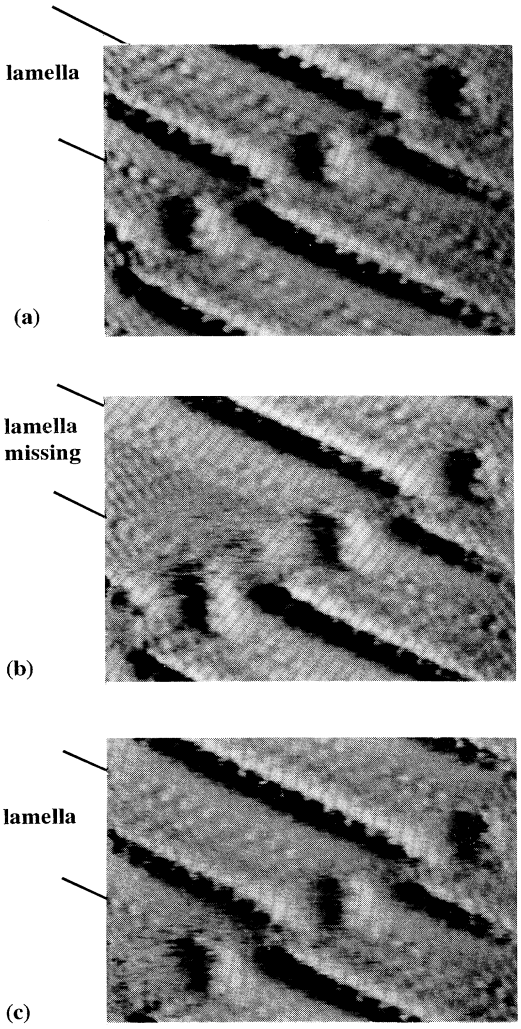

FIG. 4. Cooperative molecular motion around packing defect, illustrated by snapshots of a video recording of STM images. Image (a) shows a densely packed monolayer with two domain boundaries of the type described in Fig. 2. In (b) one of the three lamellae in the middle domain has grown by one molecule, which does not allow the adjacent lamella in the upper domain to pack properly. The model is given in Fig. 5. This defect is the reason for a "free volume" in the two-dimensional layer, which can easily diffuse, as shown in (c), where it has moved down one lamella. The time elapsed between the given snapshots is a few seconds each. Image sizes: 10.0 nm×7.5 nm.

Figure 4 displays a series of snapshots for a case where a "free volume" diffuses through the crystalline monolayer. Initially a densely packed monolayer with two domain boundaries of the type given in Fig. 2 is observed [Fig. 4(a)]. Then one lamella in the middle domain is extended by one molecule, for example by the shift rotation of one molecule in the adjacent domain. As a consequence there is not enough space now for the lamellae in the adjacent domain to pack properly [Fig. 4(b)]. The result is a free volume in the monolayer, probably filled by more mobile solvent molecules. Evidently, this situation is not very stable, and the defect diffuses around on the time scale of seconds. For example, in Fig. 4(c) it has moved down one lamella. Given in Fig. 5 is the model for the free volume in Fig. 4(b).

The two cases described in Figs. 3 and 4 above have demonstrated that the molecular dynamics at the domain boundaries can be observed by STM. It may be asked now whether similar dynamics also occurs in the extended lamellae. In order to address this question we have examined the alkane dotriacontane, which exhibits very large domains with lamellae in which the molecules are extended and lie flat on HOPG.[10] Figure 6(a) shows a molecularly resolved STM image of the center part of a lamella. Individual chains are resolved with a separation between them of 0.43 nm and a repeat unit along the chain of 0.25 nm, corresponding to two methylenes. While such an image may be stable on a time scale of many seconds, it happens that defects involving individual molecules occur, which then may diffuse through the lamellae or heal out again. Figure 6(b) is a snapshot during the diffusion. A possible explanation for the defect is the rotation of the molecule around its long axis by 90°. In the stable close-packed monolayer all alkyl zigzag planes can be expected to be perpendicular to the HOPG plane, since then the interchain spacing is consistent with the intermolecular spacings known from

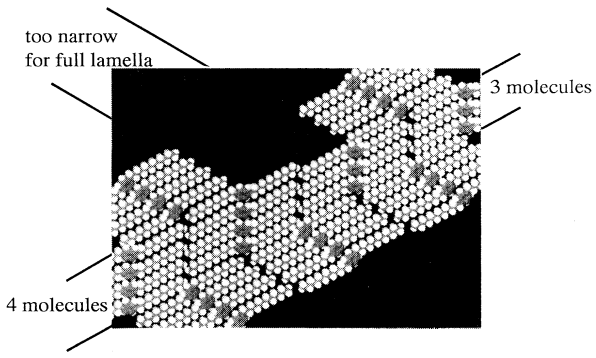

FIG. 5. Molecular model of the packing defect in Fig. 4(b).

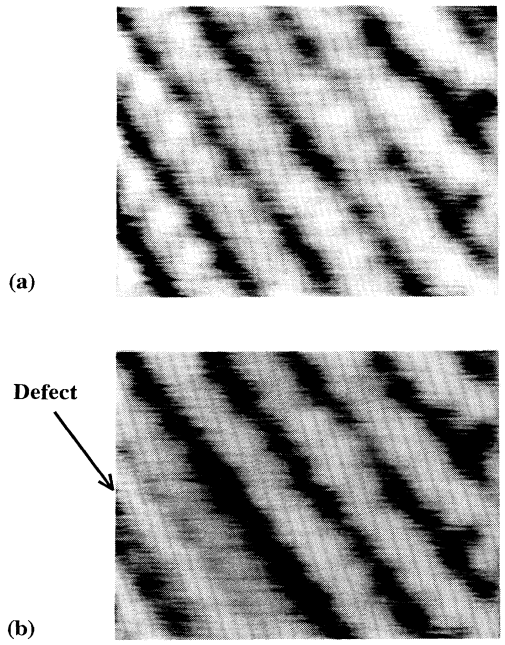

FIG. 6. STM image of the center of a lamella of the alkane dotriacontane adsorbed at the interface between an organic solution and HOPG. Image (a) shows equally spaced parallel-lying molecules. A few seconds later a defect involving an individual chain appeared at the upper right corner and diffused on the time scale of seconds down the lamella. Given in (b) is a snapshot shortly before the defect disappeared at the lower left corner. Image size: 2.0 nm × 1.6 nm.

three-dimensional alkane crystals. However, if one molecule rotates by 90° it takes more space, causing some tension in the monolayer. Evidently, this is not a stable situation. It can be expected to even lead to exchange with the ambient solution, consistent with the complete reversibility of the adsorption of alkanes.[13]

In summary, we have, for the first time, observed molecularly defined defects and dynamics in an organic monolayer, adsorbed at the solid-fluid interface. It is demonstrated that despite a very high degree of order in the monolayer there is considerable molecular dynamics possible. Clearly, STM is unique in determining both structure and dynamics in nanocrystalline monolayers on the submolecular scale.

This project has been supported by the Bundesministerium für Forschung und Technologie under the title "Ultrathin Polymer Layers" 03M4008E9 and the European Science Foundation (Additional Activity: Chemistry and Physics of Polymer Surfaces and Interfaces). S.B. acknowledges support through a Kekulé scholarship, granted by the Verband der Chemischen Industrie.

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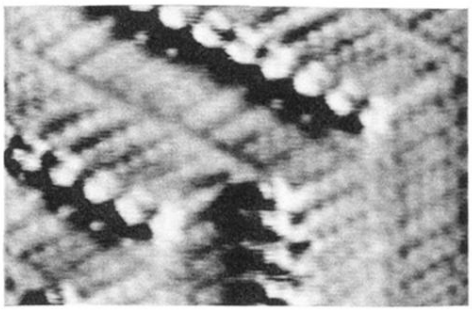

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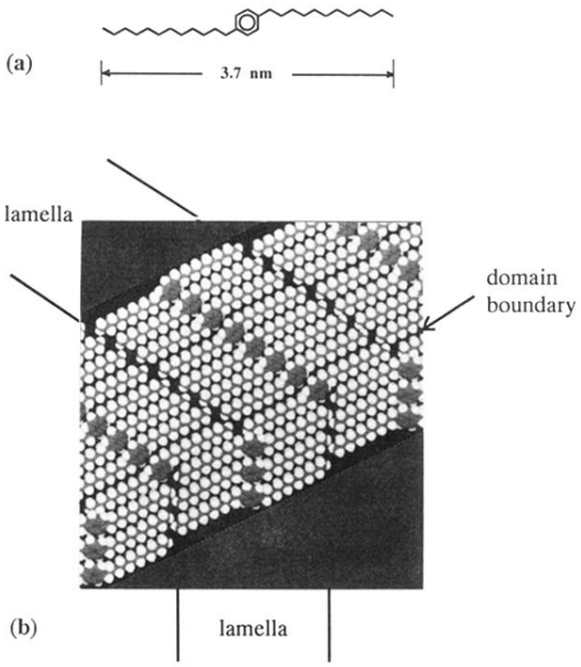

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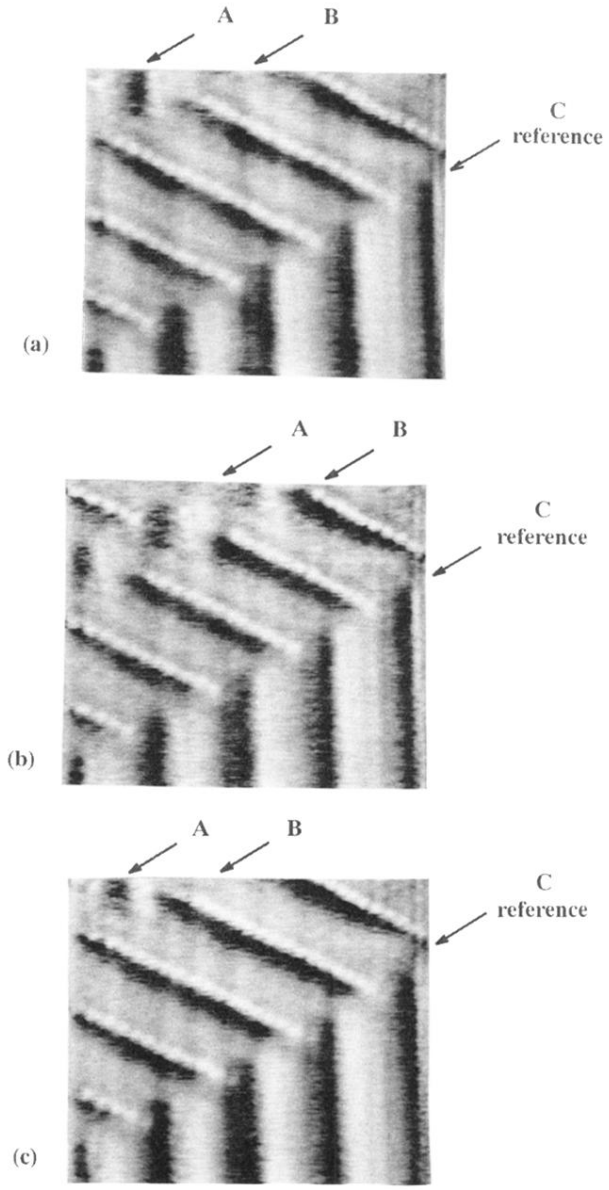

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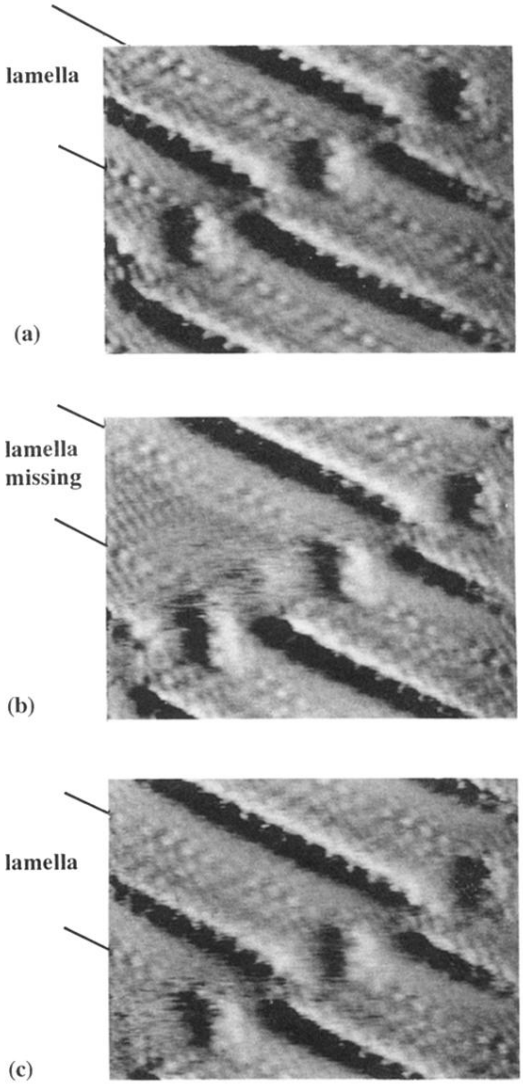

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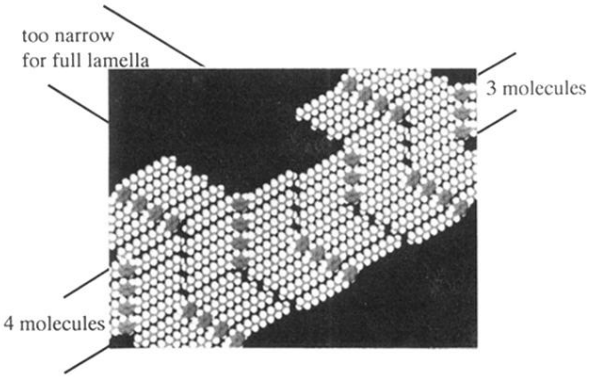

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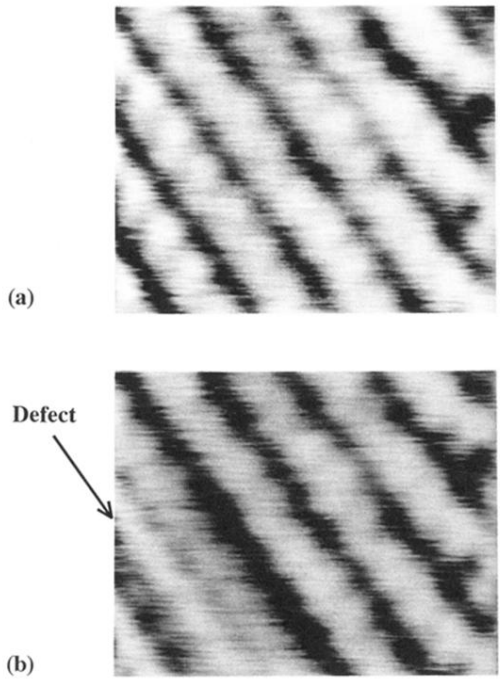

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