STM investigations of an alkane-metal-system ($C_{32}H_{66}$/In)

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Summary

Dotriacontane ($C_{32}H_{66}$) monolayers deposited on highly oriented pyrolytic graphite (HOPG) were investigated with scanning tunnelling microscopy (STM) under ambient conditions. High resolution images of dotriacontane molecules were obtained in solution. For the first time, STM investigations revealed the domain structure (lamellar structure) of $C_{32}H_{66}$ in the dried down state (after removing all excess solution). The results show, that the resolution of the dried down monolayers seems to be lowered compared to the images obtained in solution. The domain forming short-chain alkanes on HOPG were used as oriented substrates to investigate the overgrowth of evaporated indium (In). STM images show the morphology of In crystallites on the alkane substrate clearly. The simultaneous imaging of $C_{32}H_{66}$ and In was hampered, presumably owing to the different quantum-mechanical tunnelling conditions of the alkane substrate and the metal deposit.

Introduction

During recent years scanning tunneling microscopy (STM) [1] has become an important experimental method for real space imaging in the field of organic thin films and monolayers. A number of STM experiments were carried out to investigate short organic molecules, polymeric macromolecules and biological substances. Examples of these STM investigations include imaging of short-chain alkanes [2-6], ultra thin thermoplastic polymer films [7-9], liquid crystals [10] and biological materials (recA-DNA) [11]. The STM is well suited to this field of research since it has a unique surface sensitivity, i. e. the capability of directly imaging the local electronic structure and the surface morphology.

In general, these experiments were carried out with pure and "homogeneous" materials. In some cases, additional substances, e. g. solvents, were needed to enable imaging in the STM. Over and above that, STM imaging of inhomogenous systems would lead to a better understanding of interfacial properties, e. g. adhesion and/or orientation of a material in contact with an other material, as for example in composite materials.

Polymer-metal composites are materials of special scientific interest since some of them show an orientational relationship (epitaxy) between the lattices of the semicrystalline polymers and the metals [12], which is still not fully understood.

Here we present STM images of the short-chain alkane dotriacontane ($C_{32}H_{66}$) in the *dried-down state* deposited onto HOPG used as oriented substrates to investigate the mechanics of the overgrowth of evaporated In. This is a low melting metal well-known to show crystallographically oriented overgrowth (epitaxy) on different highly oriented polymer substrates [12]. $C_{32}H_{66}$ was chosen as the substrate because STM images in solution had already been obtained by McGonigal et al. [2] and other authors [3-6]. Alkane monolayers may serve as a model surface (substrate) for the study of alkane / In epitaxy since they can be imaged by STM with true molecular resolution. However, it is essential to remove any excess solution from the alkane monolayers on HOPG in order to evaporate the metal on the alkane layer under high vacuum conditions.

Experimental

The initial STM experiments were performed with commercially available dotriacontane (C32H66). The dotriacontane was dissolved in n-decane (1.6 mg/ml) and some droplets of this solution were then deposited onto a freshly cleaved surface of highly oriented pyrolytic graphite (HOPG) of ZYA grade. Subsequently, the HOPG surfaces were completely dried down by removing excess solution using a fine pipette. Highly absorbent filter paper was used to remove remaining the solution. This procedure was repeated several times until the HOPG surface appeared completely dry in an optical microscope (magnification 40 x).

In was evaporated onto the samples at room temperature in a commercial evaporation chamber at a pressure of ~ $5 \cdot 10^{-5}$ Pa. Metallic films were deposited to a nominal thickness between 0.5 nm and 5 nm at a deposition rate from 0.01 nm/s to 0.5 nm/s, monitored with a quartz crystal oscillating microbalance.

A WA Technology STM (Cambridge, UK) operating in the constant current mode was used for the investigations. The STM experiments were carried out under ambient conditions using mechanically cut gold tips. Image acquisition times ranged from 30 seconds to 1 minute. All images presented are flattened and unfiltered.

Results and Discussion

Earlier STM investigations of $C_{32}H_{66}$ dissolved in n-decane and physisorbed on HOPG have shown molecular lamellae with a width of 4 nm [2]. This value corresponds to the length of a fully-extended $C_{32}H_{66}$ molecule. The rows are shifted by half an intermolecular distance to each other. Depending on the imaging conditions, the underlying graphite lattice can appear simultaneously in the STM images to allow precise measurement of the intra- and intermolecular distances. Fig. 1 shows an example for a STM image of a $C_{32}H_{66}$ monolayer adsorbed on graphite *without* removing of the excess solution. This image may be compared to the images obtained after removing the excess solution.
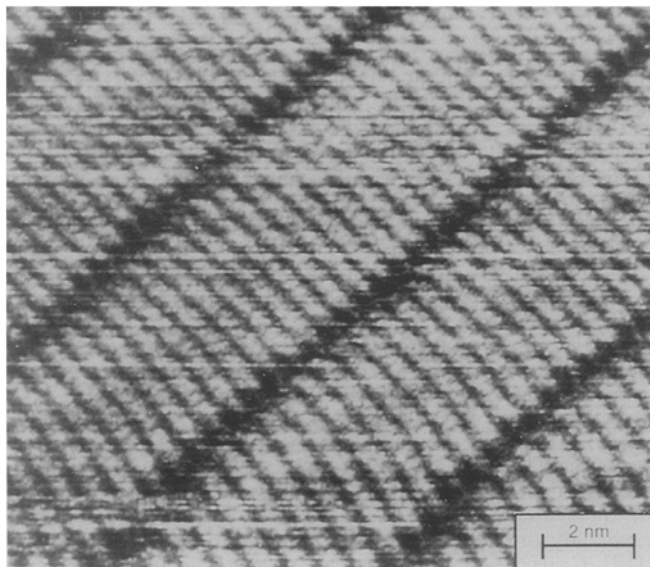

Fig. 1: *STM image of $C_{32}H_{66}$ adsorbed onto HOPG. The image was taken in solution. Image size 15 nm x 15 nm; $V_t = 300$ mV, $I_t = 100$ pA. Individual dotriacontane molecules within the lamellae can be distinguished.*
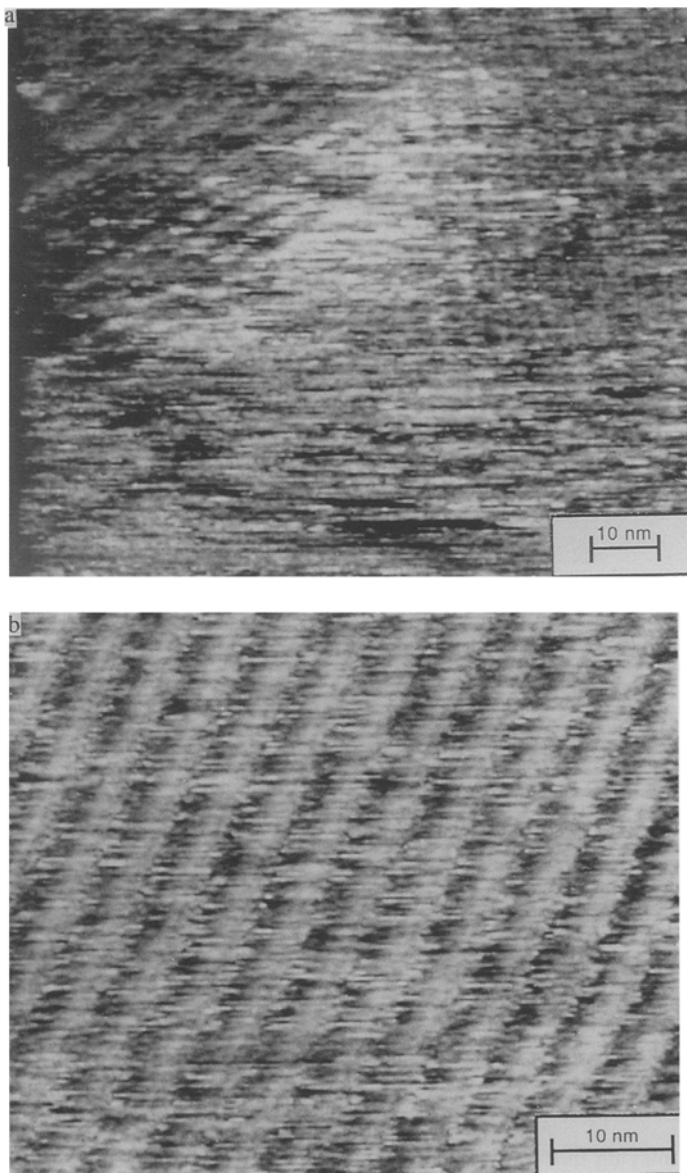
Fig. 2a and b: *(a) STM image showing three orientations of alkane lamellae upon an HOPG substrate. The lamellae which run parallel to the scan direction (at the bottom of the image) are the least distinct. Image size 100 nm x 100 nm; $V_t = 300$ mV, $I_t = 100$ pA. (b) Higher magnified image of one of the domains. The lamellar spacing was determined to be 4 nm. Image size 60 nm x 60 nm; $V_t = 300$ mV, $I_t = 100$ pA.*

Initially, unevaporated samples of dried down $C_{32}H_{66}$ deposited onto HOPG were investigated with the STM. A typical image of the sample is shown in Fig. 2a and b. In Fig. 2a, the $C_{32}H_{66}$ chains are ordered in domains with three different orientations, corresponding to the three-fold symmetry of the basal planes of the underlying graphite lattice. In the domains the $C_{32}H_{66}$ chains are oriented parallel to the graphite surface. As Fig. 2a shows, the domain which is oriented parallel to the scanning direction of the STM tip appears indistinct.

Fig. 2b shows a higher magnification of a $C_{32}H_{66}$ domain. Surprisingly, it was possible to image these domains in the dried-down state in absence of a solvent. Nevertheless, the resolution in the dried-down state seems to be poorer than the resolution in solution because it was not possible to image single $C_{32}H_{66}$ molecules. A possible explanation for this effect may be the crystallisation of dotriacontane molecules which are not removed by pipette and filter paper. This may decrease and limit the image resolution. Furthermore, the thermal stability during STM imaging of dotriacontane in solution seems to be increased compared to the imaging in the dried-down state of dotriacontane.
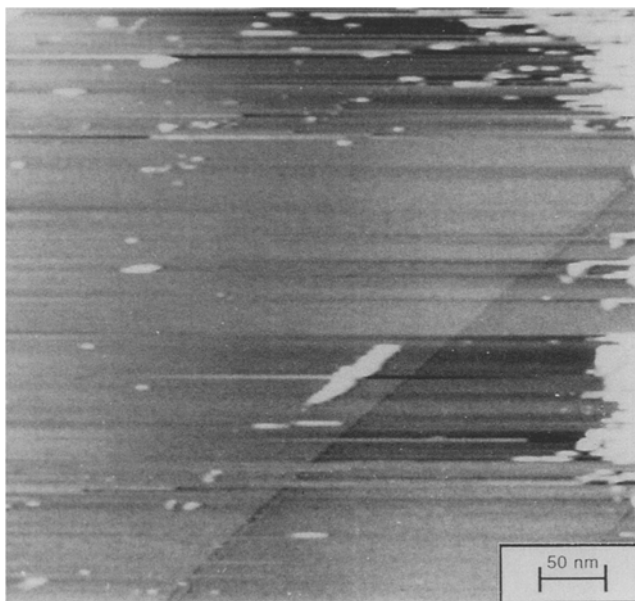
Fig. 3: *STM image showing In crystallites evaporated onto a dried-down alkane monolayer. Image size 500 nm x 500 nm; $V_t = 600$ mV, $I_t = 10$ pA. A 'window' almost free of In crystallites (see image centre) has been created due to two previous scans of 200 nm x 200 nm and 300 x 300 nm at a higher tunneling current of 100 pA. The alkane lamellae were not visible at either extremes of tunneling conditions. The brightest regions in this image represent a height of 8 nm.*

When imaging In evaporated samples, images such as that in Fig. 3 were obtained. The image shows In crystallites of different morphologies at the substrate surface. Their average diameter and height was determined to be 20-50 nm and 10 nm, respectively. Some In crystallites decorate a surface step of the underlying HOPG substrate. As deducible from the bright horizontal lines parallel to the scanning direction in Fig. 2, some of the In crystallites are swept away from the image area as a result of the scanning action of the STM tip. This observation indicates the crystallites adhere only weakly (physisorption) to the $C_{32}H_{66}$ substrate. Frictional and/or capillary forces may be responsible for this In removal process. On repeated scanning of the tip, it was possible to produce an area ("window") from which most of the In crystallites were removed. Nevertheless a few In crystallites are discernible as bright

spots and clusters on the surface. Further scanning of the surface removed all of the In crystallites.

The dotriacontane substrate and the deposited In crystallites could not be imaged simultaneously. The reason for this observation may be the different quantum-mechanical tunneling conditions, e. g. different work functions and/or different electronic energy levels [13,14] for the alkane-tip and In-tip systems, respectively.

Conclusions

1. For the first time, it was possible to image the domain structure of $C_{32}H_{66}$ by STM in the so called dried down state (after removing the excess solution). However, the image resolution of the dried down dotriacontane physisorbed monolayers deposited onto highly oriented pyrolytic graphite seems to be lowered compared to imaging in solution, presumably owing to the crystallisation of dotriacontane molecules which are not removed by pipette and filter paper.

2. STM investigations of In evaporated dotriacontane substrates show the morphology of the overgrown In crystallites. Imaging of the In crystallites by STM was possible despite the fact that they were deposited on a monolayer of (insulating) dotriacontane. The In crystallites can be easily swept away from surface areas by the scanning motion of the probe, owing to the weak interaction between the substrate surface and the deposit. It is assumed that the In crystallites are weakly physisorbed on the substrate surface.

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