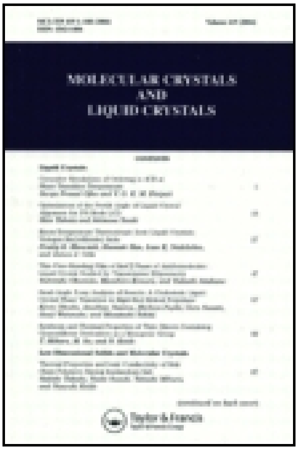

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SCANNING TUNNELING MICROSCOPY STUDY OF FULLERENE THIN FILMS ON Au(111)

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Abstract The surface of $C_{60/70}(111)$ thin films on Au(111) has been investigated by scanning tunneling microscopy (STM). Two types of ball-shaped molecules – differing in diameter and corrugation, C_{60} and C_{70} – build up a hexagonal lattice. The C_{70} content in the films, determined by counting the C_{70} molecules in the STM images, corresponds well to the C_{70} content determined by high pressure liquid chromatography on hexane solutions of the fullerene powders. STM images show lattice defects such as vacancies, interstitials, twin- and stacking boundaries. Dynamic motion of C_{70} molecules is observed. Different submonolayer coverages are documented by STM images as a function of film deposition time.

INTRODUCTION

Highly-ordered fullerene thin films can be easily prepared by sublimation of fullerene powder in a vacuum. Scanning tunneling microscopy (STM) has recently been applied to study the surface structure of fullerene thin films on metals and semiconductors in air or in ultrahigh vacuum [1–5]. The observed molecular arrangement fits well to the room-temperature structure of solid C_{60} (fcc with a nearest-neighbour-distance of 1 nm) [6]. In this paper, different types of lattice defects in fullerene thin films are discussed and a local value for the C_{60} / C_{70} ratio is determined from STM images.

EXPERIMENTAL

Very thin fullerene films (thickness: a few monolayers of $C_{60/70}$) have been prepared by sublimation of fullerene powder at 350-370 °C in a vacuum of 10^{-3} Pa onto a flame-annealed, mica supported Au(111) thin film substrate. The substrate temperature during sublimation is 220-230 °C. Three different fullerene mixtures obtained from different suppliers [7] have been studied (see Table I).

STM was performed in air at ambient temperature and pressure with mechanically prepared $Pt_{90}Ir_{10}$ tips. Typical applied bias voltages and tunneling currents were 0.1 – 0.3 V and 0.5 – 2 nA, respectively. All images were recorded in the constant current mode and represent topographic height information encoded to a grey-scale.

High pressure liquid chromatography (HPLC) was performed on hexane solutions of the fullerene powders (completely dissolved) to determine the C_{60} / C_{70} ratio prior to sublimation. The details can be found elsewhere [8].

RESULTS AND DISCUSSION

The surface structure of $C_{60/70}$ thin film samples can be imaged in real space by STM provided the films are only a few monolayers thick. The images indicate that the crystalline $C_{60/70}(111)$ domains extend over the full expanse of the Au(111) substrate terraces (several hundred nanometers in diameter). The individual fullerene molecules build up a hexagonal lattice with a nearest-neighbour-distance of 1 nm. A three-dimensional (3D) view of a $C_{60/70}$ film surface is shown in figure 1. Two different kinds of molecules are distinguished in films prepared by sublimation from

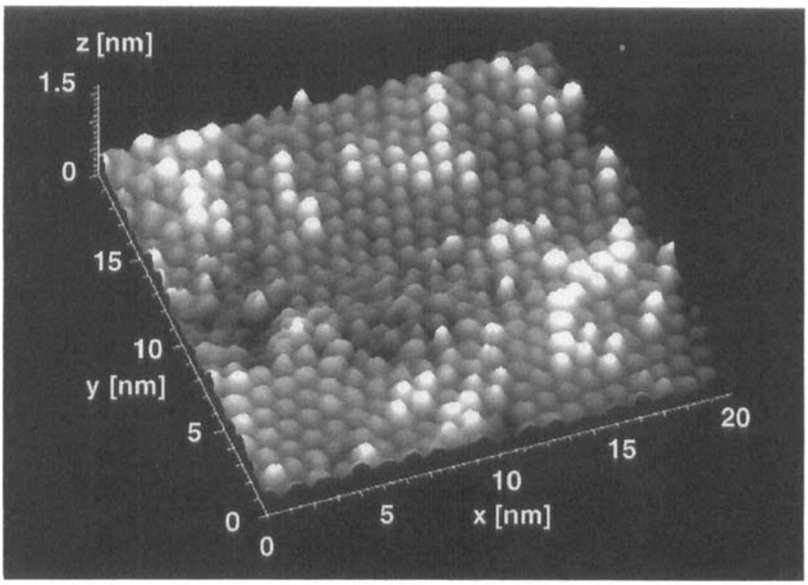

FIGURE 1. 3D-STM image of a fullerene thin film prepared by sublimation from $C_{60/70}$ powder. The two species of molecules differing in diameter and corrugation are assigned to C_{60} and C_{70} molecules. The nearest-neighbour-distance between molecules is 1 nm.

a mixture of C_{60} and C_{70} powder. They differ in size (apparent diameters: 0.7 and 0.8 nm) and corrugation (peak-to-peak values: 0.3 and 0.5 nm). In a rather straightforward assumption the molecules appearing larger are identified as C_{70} molecules, whereas the smaller ones are assigned to C_{60} molecules. The larger size and corrugation of the C_{70} molecules might be explained by their rotational motion averaged over time in the STM images. By counting the imaged C_{60} and C_{70} molecules, a local C_{60} / C_{70} ratio can be inferred. We have performed this analysis on $C_{60/70}$ films prepared under the same conditions (temperature, pressure, duration of sublimation) from three different $C_{60/70}$ powder sources [7] (with different C_{60} / C_{70} ratios).

For each $C_{60/70}$ source, STM images of different regions on the film surface were evaluated, the C_{70} content determined, averaged and the standard deviation calculated. Since the vapour pressures of C_{60} and C_{70} are dissimilar [9], it is not to be expected that the C_{60} / C_{70} ratio in the powder be accurately transferred to the sublimed film. A HPLC determination of the C_{60} / C_{70} ratio in hexane solutions of the corresponding fullerene sources yields in all three mixtures a slightly higher value for the C_{70} content than observed in the STM images (Table I). The HPLC values determined from peak integration have been corrected for molar absorptivities of C_{70} and C_{60}, $\epsilon(C_{70})/\epsilon(C_{60}) = 1.2$ at 280 nm [10]. The results for the C_{60} / C_{70} ratios are compiled in Table I.

Surfaces of fullerene thin films exhibit numerous point defects and boundaries. Two types of point defects are observed in fig. 2: a vacancy (close to letter V in fig. 2b) and a split interstitial (two C_{60} molecules on a single, regular lattice site in the center of the black circle in fig. 2b). Note that this interstitial is present in the whole series of STM images in fig. 2. These images have been recorded from a $C_{60/70}$ film (prepared from mixture 3, see Table I) at a time interval of 15 s between images. Again, the molecules appearing brighter are C_{70} molecules. Dynamic rearrangement of C_{70} molecules is observed with time. A C_{60} molecule close to the position marked with 1 in fig. 2a is replaced by a C_{70} molecule in fig. 2b. In fig. 2a and 2c, a C_{70} molecule is observed close to position 2, whereas this lattice site is occupied by a C_{60}

TABLE I. C_{70} content of different fullerene mixtures.

	mixture 1	mixture 2	mixture 3
HPLC (corrected values)	19.4 %	18.2 %	23.6 %
STM (averaged values)	15.3±2.1 %	16.6±3.7 %	20.4±3.9 %

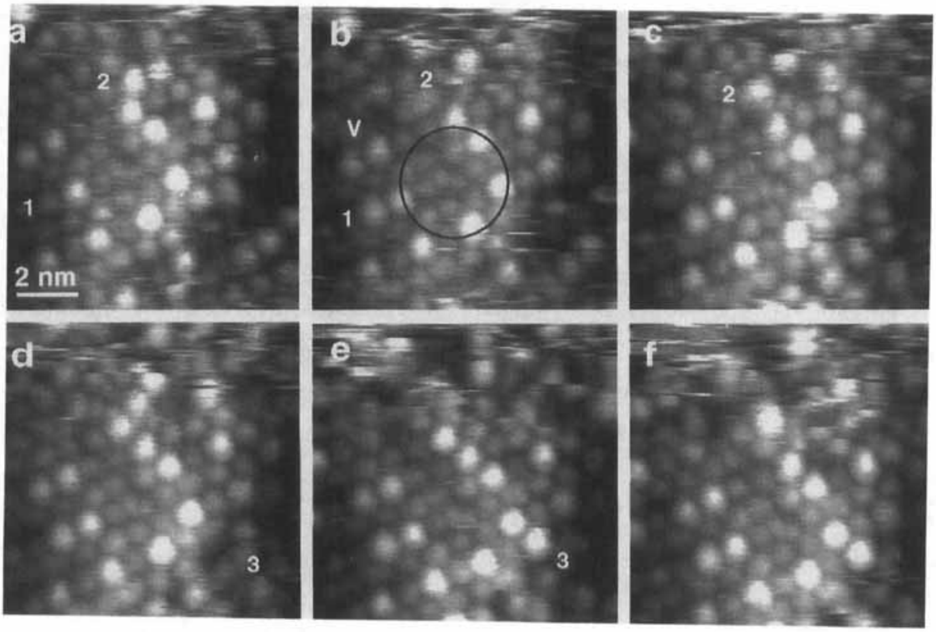

FIGURE 2. (a)-(f). Sequence of 6 STM images recorded at time intervals of 15 s showing rearrangement of C_{70} molecules and vacancies (marked by 1,2,3). Two types of lattice point defects are indicated in (b): a vacancy V and a split interstitial (center of the circle).

molecule in fig. 2b. A vacancy close to position 3 in fig. 2d is occupied with a C_{70} molecule in fig. 2e. This rearrangement might be either due to thermal diffusion or is caused by the STM tip. Two further types of lattice defects are observed in fig. 3: twin boundaries and stacking boundaries. The two domains shown in fig. 3a are separated by a twin boundary. The white lines indicate one of the <110> directions

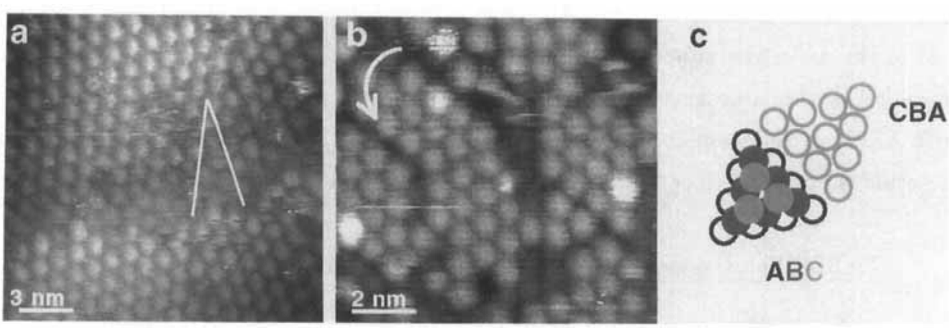

FIGURE 3. (a) Twin boundary in a C_{60} thin film. The white lines indicate <110> directions of the two lattices. (b) Stacking order boundary separating a ABC stacked domain from a CBA stacked domain. (c) Model of a stacking order boundary.

TABLE II. Preparation times for submonolayer films.

Film	a	b	c	d	e	f
Sublimation time [min]	5	15	75	125	135	145
Coverage [ML]	0.03	0.27	0.37	0.64	0.86	1.06

in the two lattices. The acute angle between the lines is close to the value of 30 degrees expected for a twin boundary.

Figure 3b shows a stacking order boundary (marked by an arrow). Such boundaries occur when domains of different layer stacking (ABC and CBA) meet. Figure 3c schematically shows a model for such a boundary (the A layer is shown in black, the B layer in dark grey and the C layer in light grey). The existence of both types of boundaries is evidence for epitaxial growth of $C_{60/70}$ on Au(111) implying a well-defined growth relation between Au(111) and $C_{60/70}$(111).

Figure 4 shows STM images of six C_{60} films prepared with different sublimation times, and hence with different coverages. Films a-e (figs. 4a-e) show a coverage of less than one monolayer (ML) of C_{60}, whereas a second layer (arrow) is observed for film f (fig. 4f). The sublimation times and coverages (determined by counting the C_{60} molecules in the STM images) are compiled in Table II. The sublimation and substrate temperatures are mentioned in the experimental section.

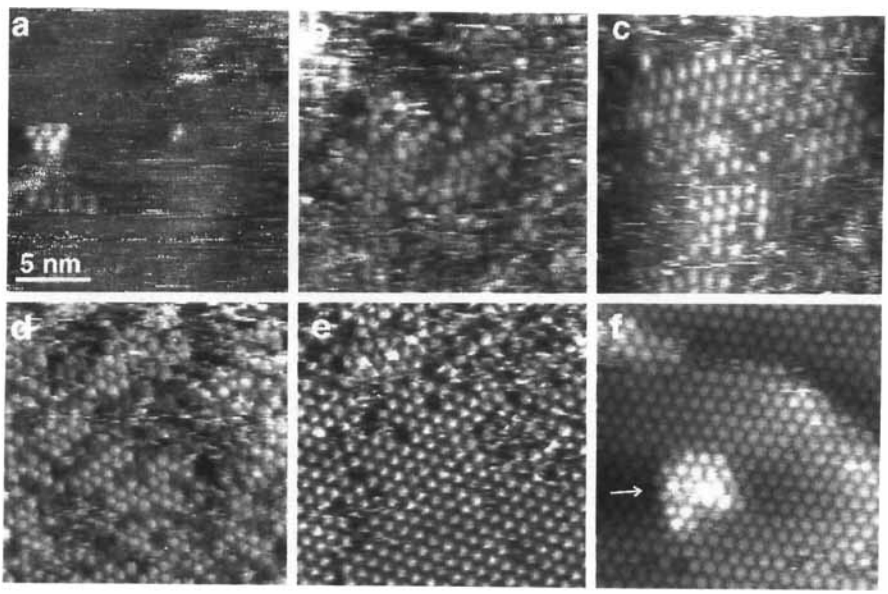

FIGURE 4. (a)-(f) C_{60} films at different coverages. The preparation conditions are compiled in Table II.

CONCLUSION

STM has proven to be a valuable tool for the local investigation of fullerene thin film surfaces with molecular scale resolution. The observed surface structure of the films (molecule layers with vacancies, interstitials, twin and stacking boundaries) allows conclusions about the epitaxy of $C_{60/70}(111)$ on Au(111). STM images of films with sub-monolayer coverage provide further evidence for the layer growth of these materials.

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