

## Decompositional Incommensurate Growth of Ferrocene Molecules on a Au(111) Surface

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(Received 30 July 2005; revised manuscript received 28 March 2006; published 21 June 2006)

Deviating from the common growth mode of molecular films of organic molecules where the adsorbates remain intact, we observe an essentially different growth behavior for metallocenes with a low temperature scanning tunneling microscope. Ferrocene molecules adsorb dissociatively and form a two layer structure. The top layer unit cell is composed of two tilted cyclopentadienyl (cp) rings, while the first layer consists of ferrocene molecules and cp-Fe complexes. Surprisingly a fourfold symmetry is observed for the top layer while the first layer displays threefold symmetry elements. It is this symmetry mismatch which induces an incommensurability between these layers in all except one surface direction. The top layer is weakly bonded and has an antiferromagnetic ground state as calculated by local spin density functional approximation.

DOI: [10.1103/PhysRevLett.96.246102](https://doi.org/10.1103/PhysRevLett.96.246102)

PACS numbers: 81.15.Aa, 61.66.Hq, 68.37.Ef, 81.07.Pr

The discovery of ferrocene  $\text{Fe}(\text{C}_5\text{H}_5)_2$  in 1951 and its structural elucidation by two separate research groups in the following year marked the birth of contemporary organometallic chemistry [1]. Metallocenes are composed of a metal atom in between two planar aromatic ligands. Their application as catalysts and organometallic polymers with magnetic properties has received considerable interest over the past two decades. In view of the development of molecular electronics these molecules are expected to exhibit unique properties, e.g., by use of magnetic atoms to exploit spin dependent effects or for the production of metal-molecule layers. The growth of highly ordered films, i.e., ultrathin molecular crystals, is receiving intense research interest [2–5], giving insight into chemical and biological processes [6] and the physical processes occurring in organic luminescence displays and solar cells. Little is known here about the growth of the first monolayer depending on a delicate balance of noncovalent interaction of the overlayer with the substrate and of the molecules in the overlayer. Depending on the charge transfer between molecule and substrate the metal-ligand bond can fragment as is the case for the system presented here.

Although metallocenes are often used for chemical applications, few studies have dealt with their crystal growth or, in particular, with the thin film growth. By use of indirect methods several first layer structures have been suggested. More specific photoemission spectroscopy and electron energy loss spectroscopy (EELS) measurements have suggested that on a Ag(100) surface ferrocene molecules adsorb molecularly with the molecule's axis perpendicular to the surface [7] while on a Cu(100) surface the molecule's axis is proposed to be parallel to the surface plane [8]. For nickelocene several tilted configurations have been suggested [9,10]. Ferrocene molecules are stable at room temperature but bind weakly to metal surfaces only at temperatures below 250 K. Upon postannealing the molecule decomposes and isolated cyclopentadienyl (cp)  $\text{C}_5\text{H}_5$  rings can be found on the surface as shown by EELS

[11–13]. We show in this Letter that ferrocene molecules already adsorb dissociatively on a Au(111) substrate at low temperatures and form a two layer structure. The metal-ligand bond breaking depends on the ligand-substrate bond and therefore the observed growth mode is expected to occur on metal surfaces if the surface electron density is sufficiently high. The topmost layer is composed of cp rings parallel to the substrate surface while the first layer is a more densely packed structure of ferrocenes and cp-Fe complexes. The topmost layer is formed vastly independently of the first layer, exhibiting a different symmetry. We observe not only a new growth mode but this system provides at the same time a system of weakly bonded and weakly interacting molecules on an inert substrate. The fourfold symmetry of the top layer is explained by an antiferromagnetic order of the cp rings.

The single crystal Au(111) substrate was prepared in a standard procedure by consecutive sputter and annealing cycles up to 1000 K. Terraces of typically 1000 Å width were achieved with only few dislocations and contaminants. Ferrocene molecules were adsorbed by cooling the sample with liquid nitrogen to 80 K, and dosing the subliming ferrocenes through a leak valve. The ferrocene molecules were sublimed at room temperature, well below the melting point of 448 K while a decomposition of the molecules in the gas phase takes place above 673 K. A coverage of about 2/3 of a monolayer was achieved by dosing 3 L. The sample procedure needs to be performed at low temperature since the molecules desorb at temperatures above 250 K. Subsequent measurements were taken with a liquid helium cooled STM at 5 K.

Figure 1 shows well-ordered ferrocene islands on the Au(111) surface found to extend over a range of several 1000 Å with practically no defects. Additionally, areas of a first layer with smaller height are visible. The herringbone reconstruction is visible through the molecular film but not influenced by it. Two domains of a topmost layer marked with A and B can be clearly distinguished. Further domains

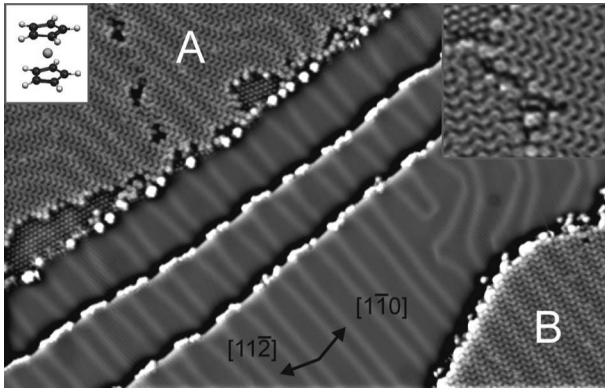


FIG. 1. Ferrocene islands with domains in the top layer and areas with only the first layer ( $820 \text{ \AA} \times 520 \text{ \AA}$ ,  $11.2 \text{ G}\Omega$ ,  $U = -1.12 \text{ V}$ ). The image is high-pass filtered to display all terraces simultaneously. The insets show a ferrocene molecule consisting of an iron atom in between two cyclopentadienyl rings and a domain boundary between A and B domains.

have been identified and it turns out that these are three rotational domains of the top layer. The islands of the ferrocene molecules are attached to the step edges and the height of the island amounts to  $4.7 \text{ \AA}$  for the top layer and  $3.2 \text{ \AA}$  for the first layer.

The top layer is an assembly of ringlike units as can be seen in Fig. 2(a) as well as in the small image of Fig. 1. The units appear with a pronounced perimeter, and they are assembled along rows with an alternating tilt. The center of the rings form a square while the apparent tilt results in a rectangular unit cell with a unit cell constant of  $a = 8.7 \text{ \AA}$ . A power spectrum from a larger area of domain A is shown in Fig. 2(b). By using Fourier transform methods their relative orientations and superperiodicities can be determined precisely.

Figure 2(c) shows a close-up of the first layer of domain A. This layer has practically a sixfold symmetry while the details of the unit cell need to be described in a rhombic unit cell. The length of the rhombic unit cell amounts to  $b = 12.4 \text{ \AA}$ . Power spectra were used to precisely measure the periodicity by numerically fitting Gauss functions to the intensity maxima.

In Fig. 2(f) the power spectra from Fig. 2(b) and 2(d) are shown together with the power spectrum of the Au(111) substrate obtained from atomically resolved images. Since triangles do not fit on squares, only one direction can have a common periodicity. Figure 2(f) shows that two marked spots coincide within experimental error for both layers, which correspond in real space to a period of the diagonal of the square in Fig. 2(a). As expected, the measured real space value  $\sqrt{2}a = 12.3 \text{ \AA}$  agrees well with  $b = 12.4 \text{ \AA}$ , the base of the rhombic unit cell in Fig. 2(c). The commensurate periodicity along this direction is shown in Fig. 2(e). By doing so any other surface direction to this direction have a ratio of  $\sqrt{3} \approx 1.732$  or a multiple

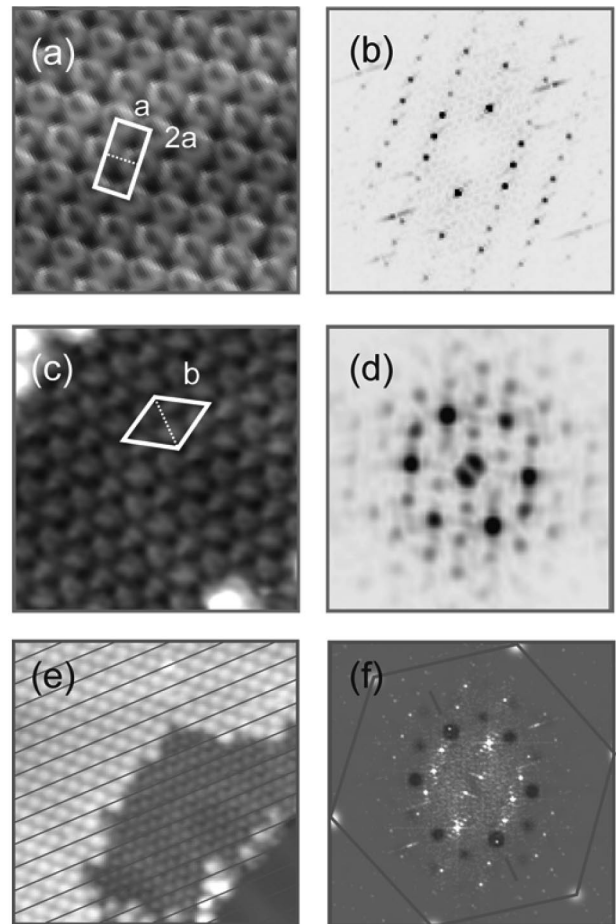


FIG. 2. (a) Image showing an area from domain A ( $62 \text{ \AA} \times 62 \text{ \AA}$ ,  $11.2 \text{ G}\Omega$ ,  $U = -1.12 \text{ V}$ ). The cyclopentadienyl rings form tilted rows with a rectangular unit cell ( $a = 8.7 \text{ \AA}$ ) while (c) the first layer has a rhombic unit cell ( $b = 12.4 \text{ \AA}$ ). (b) and (d) show the respective power spectra ( $5.1 \text{ \AA}^{-1} \times 5.1 \text{ \AA}^{-1}$ ) of (a) and (c). (f) The combined power spectra of the first and topmost layer are displayed together with the intensities from the atomically resolved Au(111) surface. Only two maxima coincide resulting in the superperiodicity as indicated in image (e).

integer of it, respectively. We note that the herringbone reconstruction is visible with an amplitude of  $\approx 0.06 \text{ \AA}$ , but apparently no moiré pattern is resolved. In summary the first layer grows epitaxially on the Au(111) surface and has a rhombic ( $\sqrt{17} \times \sqrt{17}$ ) $R12.1^\circ$  unit cell. The top layer on the other hand has a rectangular unit cell and is incommensurate in all except one direction.

To identify the building blocks of the ferrocene film the first layer was disassembled by the use of lateral manipulation. As shown in the sequence of images in Fig. 3(a), the maxima appearing in the STM images of the first layer can be converted into ringlike units with  $1.0 \text{ \AA}$  smaller height. Lateral manipulation with a closed feedback loop was used for this procedure with a voltage of  $-50 \text{ mV}$  and a tunneling resistance of  $10 \text{ M}\Omega$ . Figure 3(b) shows fragments pulled out onto the terrace by lateral manipulation. Two

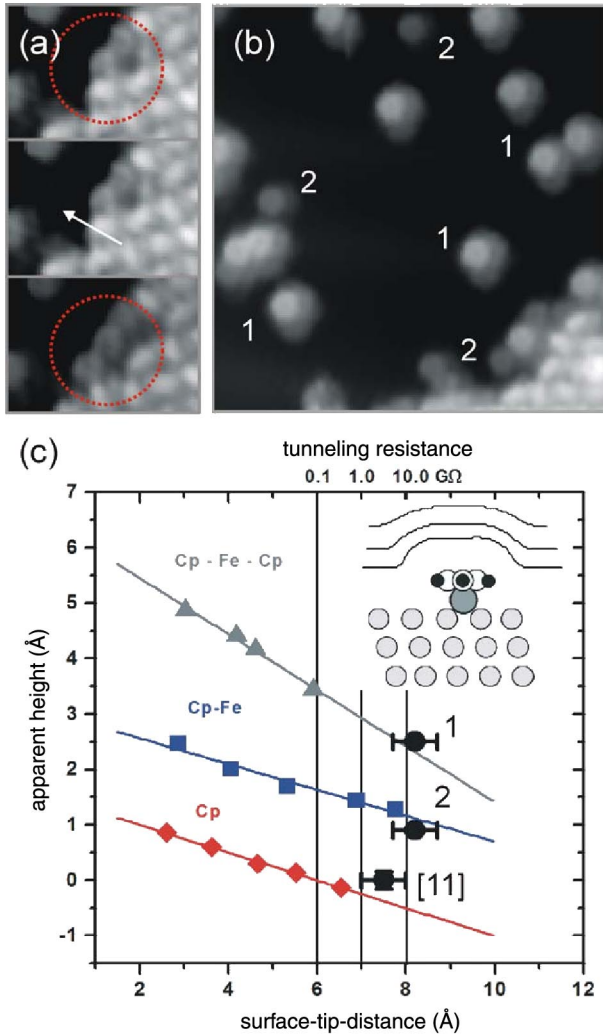


FIG. 3 (color online). (a) STM images ( $59 \text{ \AA} \times 41 \text{ \AA}$ ,  $11.2 \text{ G}\Omega$ ,  $U = -1.12 \text{ V}$ ) showing that by means of lateral manipulation a bump from the first layer can be converted into a ringlike adparticle labeled 1 in the next image (b). There the STM image ( $100 \text{ \AA} \times 100 \text{ \AA}$ ) shows the two types of fragments pulled out onto the terrace. (c) The apparent height as calculated with DFT scales linear with the surface-tip distance. The three fragments can be clearly distinguished and assigned a ferrocene molecule to type 1 and a cp-Fe complex to type 2.

types can be distinguished which both have a ringlike appearance and their measured heights amounts to 1.1 and 2.4 Å. An assignment of these heights to a ferrocene molecule or fragment of it cannot be done on the basis of structural parameters alone. We therefore have calculated the apparent height in STM images for three fragments: cp, cp-Fe complex, and a complete ferrocene molecule within density-functional-theory (DFT) and the Hamann-Tersoff-approximation [14–16]. The fragments have been adsorbed on a three layer Au(111) slab and contours of constant local density of states (LDOS) calculated for relaxed geometries. The apparent height changes as the tip-surface distance is varied since the LDOS decays

faster into the vacuum above a molecule than above the metal atoms. The result in Fig. 3(c) shows a linear dependence with the slope depending only on the ratio of the decay constants from the areas above the molecule and the metal. For comparison with the experiment, an absolute height was assigned to the used tunneling parameters as in Ref. [17]. The black circles are the experimental values which can be unambiguously assigned to a specific fragment. We therefore conclude that the first layer is composed of upright ferrocene molecules with the higher cp ring tilted. cp-Fe complexes appear attached to the ferrocene molecule if pulled onto the terrace and the upper cp ring of the ferrocene becomes horizontal.

Figure 4(a) shows the  $(\sqrt{17} \times \sqrt{17})R12.1^\circ$  unit cell of the first layer. Accordingly, the maxima in the STM topography correspond to the ferrocene molecules. The number and position of the cp-Fe complexes cannot be observed directly, but from the manipulation experiments we estimate that each ferrocene has a minimum twofold coordination with cp-Fe complexes. The proposed structure model can be seen in Fig. 4. The tilt of the upper cp rings of the ferrocene molecules is not drawn.

The top layer requires eventually an analogous discussion of the apparent height as done for the first layer. We face here a different situation though, since the first layer is terminated by molecules. We therefore expect an apparent height close to the geometric height. Additionally the observed high mobility rules cp-Fe complexes out and we conclude that the top layer consists of cp rings in accordance with their appearance.

The interaction of the ferrocene and cp-Fe complexes in the first layer is determined by strong binding to the substrate. In the top layer, on the other hand, the interaction energies are much smaller—the thermal energies at the growth temperature of 80 K are sufficient to activate diffusion on the layer and along step edges to form a well-ordered lattice. This first layer shows a topographic ampli-

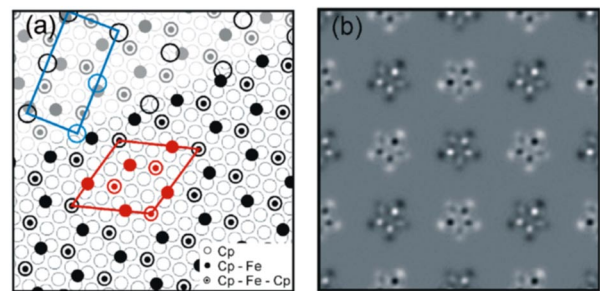


FIG. 4 (color online). (a) The full structure model for both layers and their unit cells. The rhombohedral unit cell is required to include the tilt of the cp rings—not shown here. Blue and red colors indicate the basis. (b) An isolated layer of cp rings has an antiferromagnetic ground state as calculated within local spin density functional theory. The colinear polarization  $\rho(\uparrow) - \rho(\downarrow)$  is displayed in a gray scale with 5.2 bohr magnetization per unit cell.

tude of even  $\approx 0.7 \text{ \AA}$ , but regardless of that the cp rings order independently in a squared geometry. The cp rings appear almost homogenous—a further indication that the first layer has little influence on the adsorbed cp rings of the top layer. The influence of the first layer reduces to an alignment of the top layer in one specific direction with a common periodicity. Altogether the top layer is interacting only weakly with the first layer, justifying an independent discussion of the top layer.

The observed quadratic geometry of the top layer is required for an antiferromagnetic ground state. Our DFT calculations for a two-dimensional array of cp rings show indeed that an antiferromagnetic polarization of the molecules has the lowest energy. If the gain in energy for an antiferromagnetic state superceeds the energy difference for the higher coordinated hexagonal packing geometry a squared lattice is favored. The nonmagnetic part of the cp-cp interaction, on the other hand, can give rise to a four-fold symmetry as well. We point out though that no experimental indication for that is given here since the cp rings do not have a quadratic appearance in the STM images. We hope to stimulate more theoretical and experimental work to elucidate the magnetic properties of this system.

In conclusion, we have observed the decompositional growth of ferrocene molecules on a Au(111) surface. This system displays a growth mode investigated for the first time. Ferrocene is the most strongly bonded molecule of its class. Therefore we expect this growth mode to occur also for other transition metallocenes provided that there is sufficient charge transfer to the substrate to break the metal-ligand bond. The STM proved here to be unique in the local structure clarification by gathering information which cannot be acquired with other methods. The shown results motivate further research on this class of molecule-substrate systems which needs to be extended also to other ligand systems. Finally this system constitutes a new two-dimensional system of organic magnetic molecules with a long-range antiferromagnetic ordering. Magnetic and structural phase transitions have been observed for three-dimensional molecular crystals of metallocenes [18,19], whereas we present here a system of organic radicals with the interesting possibility of a direct observation of quantum fluctuations at lower temperatures [20].

The financial support provided by the U. S. Department of Energy No. DEFG02-02ER46012 and the NSF-DMR No. 0304314 Grants are gratefully acknowledged. A

computation Grant (No. PHS0255-1) from the Ohio Supercomputing Center (OSC) and (No. DMR060005N) the National Center for Supercomputing Applications (NCSA) is gratefully acknowledged. We thank Nancy Sandler, David Drabold, and Alexander Govorov for fruitful discussions.

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