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One-dimensional chains of C_{60} molecules on Cu(2 2 1)

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Abstract

On Cu(2 2 1) it is possible to grow long ordered one-dimensional chains of C_{60} molecules aligned along the steps of this vicinal template. By scanning tunneling microscopy (STM) a unit cell with two distinctly imaged molecules is found. From distribution of the rare defects a bond energy difference of the two types of molecules is inferred. At least in one of the two species, the molecules have a well-defined orientation as determined by X-ray photoelectron diffraction (XPD).
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1. Introduction

Since the discovery of C_{60}, many studies have been performed in order to characterize the binding and the ordering of fullerenes at solid surfaces. C_{60} attracts much interest because it is an ideal model for exploring fundamental concepts in strongly correlated system as well as for its possible applications in molecular electronics. An important issue concerns the synthesis of different low-dimensional systems, where exotic phenomena are expected. In alkali metal doped C_{60} surfaces, for example, superconductivity has been observed at low temperatures. Monolayers of C_{60} on

Ag(1 0 0) even showed an excitation gap persisting up to 260 K [1]. Only recently it became possible to directly measure the band dispersion in the electron doped C_{60}/K/Ag(1 1 1) system and density functional calculations indicated that the electronic band dispersion is highly sensitive to the relative orientation of the molecules [2].

Depending on the substrate, single layers of C_{60} molecules are found in different geometrical arrangements and different bonding and charge states. On Cu(1 1 1), C_{60} molecules form an ordered (4×4) monolayer system [3]. Photoelectron diffraction showed that the molecules are adsorbed with the 6-ring towards the surface, in two azimuthally equivalent orientations [4]. In order to orient these molecules and to align them into one-dimensional chains, we grew C_{60} structures on several vicinal copper surfaces. In this paper results for C_{60} on Cu(2 2 1) are reported. The

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nominal terrace width on this particular vicinal surface is 7.66 Å, which is very close to the average diameter of a C_{60} molecule. This leads to the expectation that individual rows of C_{60} should form on the terraces. Preparing one monolayer of C_{60} on this surface, we find a highly regular close-packed pattern the unit cell of which contains two distinct C_{60} molecules. This has been identified by low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). STM images show that bright chains of molecules alternate with dimmer chains. At least in one of the two types of chains, the molecules have a single well-defined orientation as determined by X-ray photoelectron diffraction (XPD). We present a plausible structural model where the different brightness arises from the different molecular bonding to the substrate.

2. Experiment

The experiments were performed in a ultra-high vacuum system equipped with a scanning tunneling microscope and an electron spectrometer. The STM experiments were carried out with a Park Scientific microprobe VPII instrument. The images were recorded at room temperature in constant-current mode with negative sample bias using electrochemically etched tungsten tips. The photoemission measurements were performed in a VG ESCALAB 220 spectrometer modified with a computer-controlled two-axis sample goniometer [5]. The XPD pattern has been obtained using Mg Kα radiation with the sample kept at room temperature. Cu(2 2 1), the stepped surface con-

sidered in this work, is a B-type vicinal of Cu(1 1 1) that is composed of (1 1 1) terraces bound by monoatomic steps with (1 1 $\bar{1}$) step facets. The nominal terrace width is four atomic rows including the corner atoms below the step. The single crystal has been carefully prepared and characterized, as described in a previous publication [6]. C_{60} powder (99.9%) was sublimated from a titanium crucible using an evaporation rate of 0.8 ML/h as calibrated by XPS. The background pressure during evaporation was kept below 3×10^{-10} mbar. The ordered structure has been obtained by evaporating one ML of C_{60} onto the surface held at room temperature and subsequent annealing at 570 K for a few minutes. We checked the sample cleanliness and the film quality by XPS, LEED and STM.

3. Results and discussion

In Fig. 1 we present the experimental LEED patterns for the clean Cu(2 2 1) and the C_{60} monolayer measured at the same energy. In the diffraction pattern from the substrate the observed spot splitting is consistent with a regular step structure over large areas (Fig. 1(a)). The LEED optics has been calibrated using the (1 1 1) copper surface and the unit cell of the substrate was determined by comparing the separation of two consecutive step lattice spots and the distance between two diffraction spots of the flat surface. With respect to the (1 1 1) terraces, the unit cell of Cu(2 2 1) corresponds to a $(1 \times 3\frac{1}{3})$ mesh. Deposition of one monolayer of C_{60} and subsequent annealing results in the sharp LEED pattern
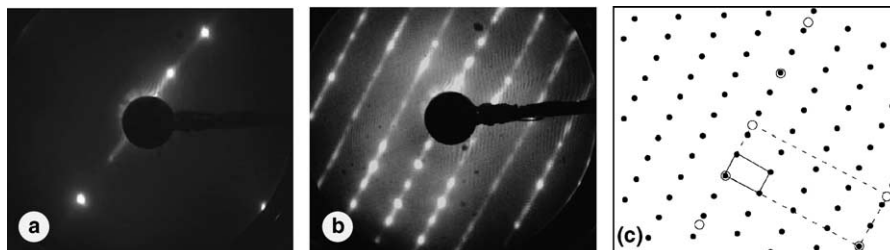

Fig. 1. LEED patterns for (a) clean Cu(2 2 1) and (b) one C_{60} monolayer on Cu(2 2 1) (electron energy = 37 eV). (c) Schematic view of the reciprocal space structure: the full line describes the overlayer unit cell, while the dashed line the unit cell of the substrate.

shown in Fig. 1(b). The periodicity along the step, 10.2 Å, agrees with the C_{60}–C_{60} distance of the 4×4 structure on Cu(1 1 1). The lattice vector in the direction perpendicular to the steps is 19.2 ± 0.5 Å. The adsorbed layer does not correspond to a simple overlayer structure: it is incommensurate to the substrate and it is compatible with a $(4 \times 8\frac{2}{3})$ unit cell with respect to the (1 1 1) terraces. Considering the dimensions of the unit cell and that the coverage corresponds to a full layer, we can argue that there are two molecules per unit cell and the area per C_{60} amounts to 97.9 Å^2. The mismatch between the unit cell of the substrate and that of C_{60} indicates substantial mass transport during synthesis of the structure. The fact that the lattice vector perpendicular to the steps is compatible with twice the step–step separation of the near-by vicinal Cu(5 5 3) surface suggests a reconstruction of the substrate.

STM measurements of one monolayer of C_{60} on Cu(2 2 1) show large terraces of about 120 Å average width separated mainly by double steps of the same height as double steps on clean Cu(1 1 1) (Fig. 2(a)). Zooming in on the terraces, it is possible to analyze the arrangement of C_{60} molecules in detail (Fig. 2(b) and (c)). The layer exhibits a quasi-hexagonal close-packed pattern and the molecules are aligned in well-ordered one-dimensional chains along the step direction of the substrate. The periodicity along the rows and the 4% expansion of the hexagonal pattern perpendicular to the steps are in agreement with the LEED measurements. On each terrace, we observe that the chains have a regular modulation in brightness and the unit cell is composed of two distinct C_{60} molecules: one appears bright and the other dim. The presence of two different kinds of molecular images, i.e., bright and dim, has been observed quite often in STM studies of C_{60} on metal surfaces. Since STM maps the topography and the local density of states, it is controversial whether the brightness difference is related to a real difference in height (i.e. molecules that are pushed out) [7,8], to an electronic effect (i.e. a spatially non-homogeneous charge transfer) [9], or to a distinct molecular orientation [10,11]. Fig. 2(d) shows two topographical profiles along the lines indicated in (b) crossing a double and a single step. The vertical
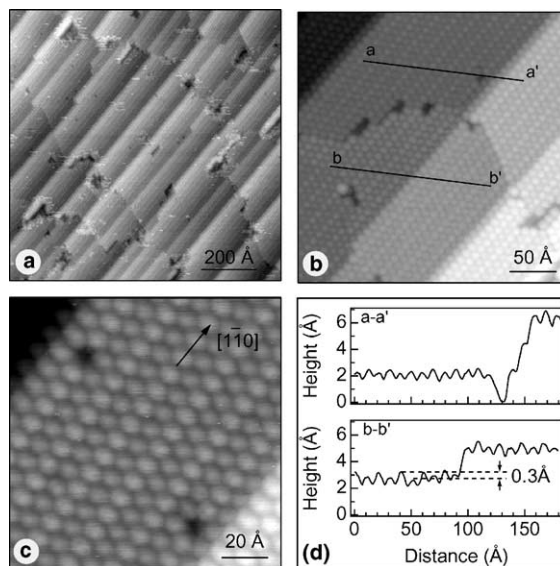

Fig. 2. Room temperature STM images from one monolayer of C_{60} on Cu(2 2 1). (a) Large terraces along the step direction of the substrate. Zooming in, it is possible to see alternating bright and dim rows of C_{60} molecules forming a quasi-hexagonal pattern ((b) and (c)). The rare defects (C_{60} vacancies) are more abundant in the bright chains. (d) Topographical profiles along the lines indicated in (b).

displacements between adjacent rows of different brightness are all measured to be 0.31 ± 0.07 Å at a bias of −1.5 V and a current of 0.5 nA. Changing the tunneling voltage or the current, this height difference shows variations of about 20%. It is thus consistent with a topographic height difference, but we cannot exclude other possible explanations. The observation that C_{60} defects, i.e., vacancies, are more likely to occur in the bright chains (the ratio between single defects in the dim and the bright chains is 3:10) supports the assignment that the two molecular images reflect different local bonding environments to the substrate. The small difference in height between molecules on different rows, only 0.31 Å, indicates that the steps of the substrate remain monoatomic and that every step is decorated by a single C_{60} molecule. For these reasons, when the tip is scanning the optical surface, the decorated steps look like large almost flat terraces. The apparent step bunches in the two profiles of Fig. 2(d) correspond to double and quadruple substrate steps. The height and the

periodicity of the step bunches is compatible with a reconstruction of the substrate into a different vicinal surface. On average we see two additional steps every 12 C_{60} rows. This is consistent with a reconstruction of the $(2\,2\,1)$ surface, with four atomic rows per terrace, to a $(5\,5\,3)$ surface, with five atomic rows, for which one additional step every six $(5\,5\,3)$-terraces is expected. The fact that we see a reconstruction of the substrate after adsorption of the C_{60} molecules is not surprising: It has been already noticed that C_{60} induces reconstruction, especially in the more open $(1\,1\,0)$ surfaces [7,8,12]. The annealing temperature of the monolayer, 570 K, was very close to the annealing temperature of the clean substrate where the adatom mobility is high; vicinal copper surfaces are known to undergo reconstructions after adsorption of some molecules such as e.g., oxygen [13].

The C_{60} structure has been further investigated by X-ray photoelectron diffraction measurements. This technique allows to determine the molecular orientation of the adsorbed C_{60} and it has been shown in other cases that the orientation of the cage is related to the different brightness of the molecules [10,14]. Fig. 3 shows the experimental C 1s XPD pattern from the ordered C_{60} monolayer
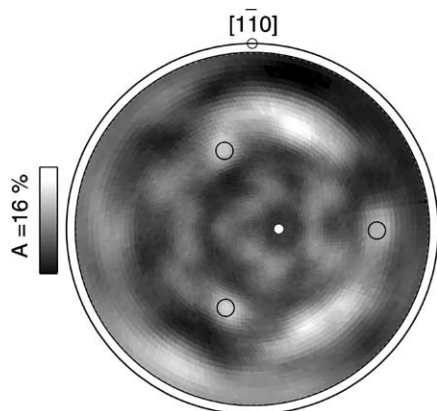

Fig. 3. Experimental C 1s XPD pattern (Mg Kα, $E_{kin} = 970$ eV). The diffraction intensities are shown in stereographic projection and on a linear grey scale with maximum intensity corresponding to white. The white point indicates the $[1\,1\,1]$ direction and the open circles the three forward focusing maxima. The direction of the substrate along the step is also reported.

grown on Cu$(2\,2\,1)$. The data were measured in the forward scattering regime ($E_{kin} = 970$ eV) and are presented as stereographic projection on a linear grey scale with maximum intensity corresponding to white. The orientation of the substrate, as determined by the XPD pattern of Cu $2p_{3/2}$ core level, is also indicated. The pattern has been normalized to the smooth polar angle dependent background typical for adsorbate emission. The diffraction anisotropy is 16%, which is typical for well-ordered C_{60} structures. This indicates that most C_{60} molecules are not freely rotating on the surface. The diffraction pattern is dominantly three-fold rotational symmetric around the $[1\,1\,1]$ direction and not six-fold symmetric as on Cu$(1\,1\,1)$. The prominent maxima indicated in Fig. 3 correspond to three interatomic directions of the molecule which are perpendicular one to the other and point out of the $(1\,1\,1)$ plane. The position of these maxima indicate that a large fraction of C_{60} molecules is lying with the hexagon on the terraces and with a preferred azimuthal orientation of the cage.

With the real space model presented in Fig. 4, which is based on geometrical reasoning, all aspects of LEED, STM and XPD data are rationalized. The molecules are adsorbed in long ordered lines along the steps of a $(5\,5\,3)$ surface. From the dimensions and the geometry of the unit cell, it turns out that two adsorption sites, with different coordination of the molecules with respects to the steps, are occupied. The observations that the defects are more frequent on bright chains, suggests that these chains correspond to molecules with lower coordination to the substrate. With the annealing temperature of the C_{60} layer, 570 K, and assuming that the probability of occupancy of the two sites is proportional to the ratio of 3:10 between single defects in the two rows, we can estimate a bond energy difference between the two sites of 59 ± 20 meV. Very likely the different coordination to the substrate is also the origin of different possible orientations of the molecules. It is reasonable to assume that the defined orientation described in the XPD pattern by the three high intensity spots corresponds to the orientation of the higher coordinated dark molecules.
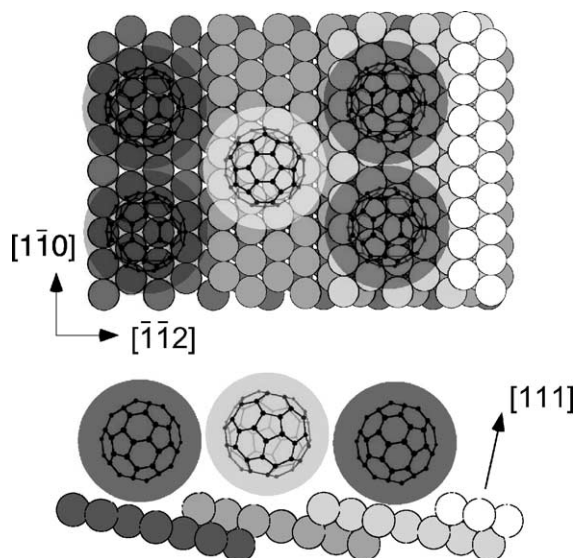
Fig. 4. Suggested real space model for the $(4 \times 8\frac{2}{3})$ structure of C_{60} on the unit cell of Cu(5 5 3). Top panel: view along [1 1 1]. The azimuthal orientation of the C_{60} molecules shown is arbitrary. The bright (dim) molecular rows seen in STM correspond to C_{60} molecules which are one (two)-fold coordinated to the ascending steps. Bottom panel: side view perpendicular to [1 $\bar{1}$ 0]. It describes the small difference in height between molecules on different terraces imaged by the STM. The circles around the C_{60} cage correspond to the van der Waals radii of the molecules.

In conclusion, the structure of one monolayer of C_{60} on Cu(2 2 1) has been studied by complementary experimental techniques. LEED and STM show a quasi-hexagonal pattern where the molecules are arranged in well-ordered one-dimensional chains. The size of the unit cell and the periodicity of the step bunches indicate a reconstruction of the substrate towards a (5 5 3) surface. The different brightness of the two rows of molecules has been discussed as different coordination to the substrate. XPD indicates that at least one of the two species of molecules aligned along the step have a defined orientation. The results have a general importance for an understanding of the interplay between adsorbate–adsorbate and adsorbate–substrate interactions.

Acknowledgement

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