Study of $C_{60}/Au(110)$-$p(6 \times 5)$ Reconstruction from In-Plane X-Ray Diffraction Data

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Fullerene molecules absorbed on the highly anisotropic Au(110)-$p(1 \times 2)$ surface induce an ordered $p(6 \times 5)$ superstructure that has been solved by applying the 2D "direct methods" difference sum function to the surface x-ray diffraction data set. We found that the C_{60}-gold interface is structurally much more complex than the one previously suggested by scanning tunneling microscopy data [J. K. Gimzewski, S. Modesti, and R. R. Schlittler, Phys. Rev. Lett. **72**, 1036 (1994)]. Indeed a large fraction of Au surface atoms are displaced from their original positions producing microscopic pits that may accommodate the fullerene molecules.

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The interaction of buckminsterfullerene C_{60} with different surfaces has attracted much interest in recent years and a surprising variety of both bond strength and bond character has been found [1]. The bonding is not only of van der Waals type as originally thought [2] and observed on surfaces like GeS [3], SiO_2 [4], or graphite [5]. On all metallic and conventional semiconductor surfaces investigated so far (Si, Ge, GaAs), fullerenes are always chemisorbed, and the degree of hybridization of the C_{60} molecular orbitals with the substrate electronic states, as well as the amount of charge transfer, differs greatly from substrate to substrate [6]. In general, the structure of C_{60} monolayers is hexagonal or quasihexagonal resulting in compressed or enlarged C_{60}-C_{60} spacings compared to the C_{60} solid in order to achieve commensurate structures [1,7,8]. Photoelectron diffraction studies [9] showed that different adsorption geometries are possible for the chemisorption case, comprising a ring, a single or double bond of the C_{60} cage, or even only a C_{60} edge atom facing the substrate, and that the adsorbed fullerenes do not rotate at room temperature. Moreover, C_{60} is also capable of inducing strong structural modifications in a metal substrate as demonstrated by a recent scanning tunneling microscopy (STM) study of $C_{60}/Ni(110)$ [10] which reveals that different adsorbate phases are formed within a general roughening and restructuring of the interface resulting in the formation of (100) microfacets.

In order to achieve a better understanding of the restructuring induced by C_{60} on metal surfaces we decided to carry out a quantitative x-ray structural investigation on a system previously studied by STM: the $C_{60}/Au(110)$-(6×5) structure [11]. The electronic properties of this system are known from previous studies [12–14], where evidence for a chemisorptive bond with metallic screening properties and charge transfer from the Au to the fullerene was found.

The clean Au(110) surface is very anisotropic since it exhibits the (1×2) missing row reconstruction [15] where one of every two closest-packed atomic rows along the $[1\bar{1}0]$ direction is missing. In the thermodynamically stable adsorption phase corresponding to a (6×5) superstructure, C_{60} forms a hexagonal close-packed corrugated layer and areas of the substrate not covered by the adsorbate show a (1×5) missing row reconstruction [11]. The corrugation of the C_{60} monolayer was comparable to the difference in height of the (1×2) and (1×3) missing row structures constituting the base of the (1×5) reconstruction leading the authors to conclude that the (1×5) Au reconstruction was also extending below the C_{60} layer.

X-ray diffraction experiments were carried out at the surface diffraction beam line ID3 of the European Synchrotron Radiation Facility in Grenoble [16]. The x-ray beam was generated by two undulators, monochromatized with a cryogenically cooled double crystal Si(111) monochromator and sagitally focused. The incident beam had an energy of 13.4 keV and dimensions, at the sample position, of 0.1 mm horizontal and 0.5 mm vertical. The Au(110) single crystal [surface plane parallel to the crystallographic (110) planes within 0.2°, as determined by x-ray diffraction measurements] was mounted in the UHV diffraction chamber (base pressure 1×10^{-10} mbar) coupled with a six circle diffractometer and equipped with several ports for evaporators, an ion sputter gun, and an Auger spectroscopy setup. The sample was heated by a resistor and its temperature was monitored by a thermocouple inserted into a hole made in the crystal. The Au(110) surface was described by lattice vectors $(\mathbf{A}_1, \mathbf{A}_2, \mathbf{A}_3)$ parallel to the $[1\bar{1}0]$, [001], and [110] directions, respectively, where $A_1 = A_3 = a_0/\sqrt{2}$, $A_2 = a_0$ ($a_0 = $ bulk lattice constant). The coordinates of the corresponding reciprocal lattice vectors were denoted by H, K, L. The diffractometer was operated at a constant

incidence angle of 2°. The integrated intensities were recorded by setting an in-plane diffraction condition and then by rocking the crystal around its surface normal.

The Au(1×2) reconstructed surface was prepared by standard sputtering and annealing cycles and exhibited reconstructed terraces with a domain size of typically 2000 Å as determined from the angular width of the x-ray reflections. Surface cleanliness was verified by Auger spectroscopy. C_{60} (purity 99.9%) was sublimed from a tantalum crucible kept at 750 K. The fullerene coverage was determined by Auger spectroscopy and calibrated recording the C/Au peak ratio after annealing a C_{60} multilayer to 500 K, a procedure which, as previously reported [12–14], results in a single adsorbed fullerene layer on the surface.

For the preparation of the (6×5) structure we tested several procedures reported in the literature. The best one, in terms of crystalline quality of the overlayer, was the following. About two layers of C_{60} were adsorbed on the Au substrate held at room temperature. After deposition a $\sim$50% decrease of the intensities of the (1×2) fractional order clean Au reflections was detected, suggesting that some of the Au atoms had moved due to the interaction with C_{60}. The film was subsequently annealed to 600 K until a well developed (6×5) structure was observable. The dimensions of the (6×5) domains were found to be typically $\sim$250 Å and the intensity of the (1×2) reflections was very weak, amounting to about 7% of their initial values. Once the formation of the reconstruction was completed, i.e., no further intensity changes were observed, the sample was cooled back to room temperature and a rather extensive in-plane fractional order data set was collected at $L = 0.2$ reciprocal lattice units.

A total of 300 in-plane fractional order reflections were measured which reduced to 130 symmetrically independent ones shown in Fig. 1 (empty semicircles). The average residual between equivalent reflections (mm "Laue" symmetry amounted to about 10%. All reflections (H, K) satisfying the condition $H = (2n + 1)/6$ and $K = 0$, where n is an integer, were found either to be totally absent or to have very small intensities which fall within their respective uncertainty range. This implies that the plane group symmetry of the surface cell must be either $p1g$ or $p2mg$.

As already recalled above, the structural model proposed by the STM study [11] consists of a hexagonal fullerene layer on top of a (1×5) reconstructed Au(110) surface. By evaluating the diffracted intensities which should result from that structure, it is found that the reflections with $H = n$ (integer) should be, on average, 25 times stronger than the others due to the (6×5) periodicity. This is clearly not the case for the data shown in Fig. 1 where the intensities of all the reflections are of the same order of magnitude and the average ratio between integer ($H = n$) and fractional reflection intensities is 1.35:1. These differences immediately rule out the model proposed on the basis
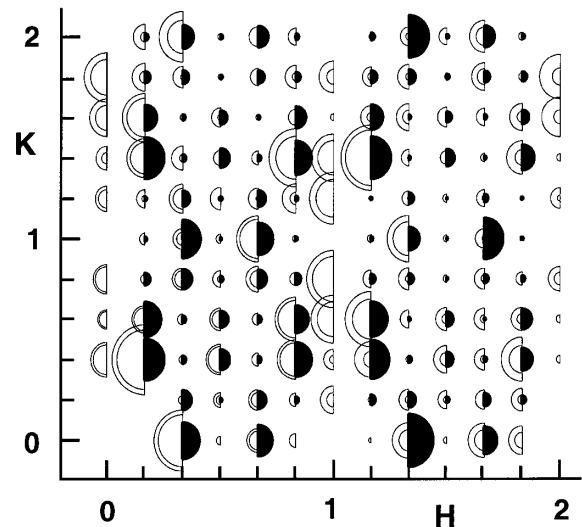

FIG. 1. In-plane structure factors amplitudes corresponding to the C_{60}/Au(110)-p(6×5) surface reconstruction. The measured values and their associated uncertainties are proportional to the radii of the two empty semicircles. The filled semicircles are proportional to the calculated values using the model shown in Fig. 3. This model was not used to calculate the values of the integer H-reflections because these data were not used in the computation of the "direct methods" δ sum function as explained in this Letter.

of the STM images. However, we explored several possibilities based on the STM model by allowing the Au atoms of the (6×5) structure to relax in the direction parallel to the surface; displacements, induced by the fullerene, could not have been detected with STM. The refinement procedure was performed considering $p2mg$ symmetry with a total of 28 structural parameters and resulted in in-plane displacements of Au atoms larger than 2 Å, with a reduced χ^2 larger than 6. These solutions were considered unrealistic and indicate that the assumed structural model is not correct. Attempts to suppress the mirror line m were not considered due to the excessively high number of variables involved.

Standard procedures routinely employed in surface crystallography resulted in being useless due to the complexity of the difference Patterson function. This type of failure is becoming a general problem in resolving the surface structure of complex adsorbate-substrate systems. New automated solution methods are then required. Promising results in this direction have already appeared in the recent literature [17–21].

The result of our analysis, following this scheme, is shown in Fig. 2 in the form of the projected δ-map (the difference between the electronic density of the reconstructed cell and its average). The computation was based on the determination of the phase values of the largest structure factors obtained by maximizing the direct methods δ sum function [22], starting from randomly assigned values, which can be written as
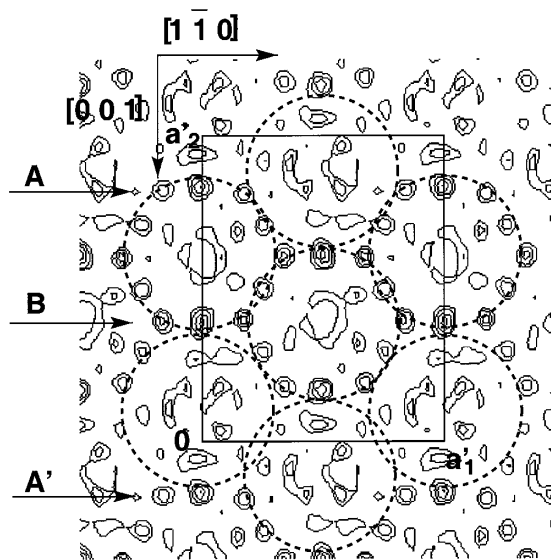
FIG. 2. Contour δ map (only positive regions) of $C_{60}/Au(001)$-$p(6 \times 5)$ obtained by applying the direct methods δ sum function to the partial set of in-plane reflections given in Fig. 1 (see text for details). Dashed circles indicate the locations of the C_{60} molecules. The rectangle is the 6×5 unit cell whose dimension is 17.3×20.4 Å^2.

$$S(\Phi) = S \int_S \delta P_0(\mathbf{x}) \, \delta P(\mathbf{x}, \Phi) \, d\mathbf{x}.$$

This function measures the coincidence between the observed 2D difference Patterson-like function δP_0 and the calculated one $\delta P(\Phi)$ given in terms of the collectivity Φ of phases of the largest superstructure reflections. This integral will be a large positive quantity if the coincidence between observed and calculated difference Patterson functions is good. The meaning of the δP function is similar to that of the standard Patterson one [22,23] and it is defined as the autocorrelation of δ function.

Maximization of the $S(\Phi)$ was achieved by using the intensities of the in-plane reflections up to a resolution of 1.2 Å assuming a pg plane group symmetry. In order to be sensitive only to the (6×5) structure and not to the (1×5) reconstruction in bare regions of the substrate which might result from a noncomplete adsorbate coverage, we have ignored all reflections with $H = n$ (integer), which are common to both structures, and considered only the noninteger reflections exclusive of the (6×5) structure. In fact, as already mentioned above (Fig. 1), the integer H reflections are 35% higher in intensity than the noninteger ones, and this suggests that some residual (1×5) regions may still exist. Figure 2 reproduces therefore the δ map computed with the phases corresponding to the solution with the best figures of merit using this subset of data.

Inspection of the stronger peaks in the δ map indicates the presence of a mirror line normal to A_1 leading us to conclude that the true in-plane symmetry is most probably $p2mg$. The highest-intensity δ peaks, i.e., the strongest distortions, are located along rings with a diameter of about

9.6 Å and centered approximately at $(\frac{1}{2}, 0.4)$ and $(0, 0.1)$ which are marked as dashed lines in Fig. 2. It is important to note that if the resolution of the calculation is relaxed to 5 Å, these strong distortions are no longer visible in the δ map and only broad features at the centers of the rings are obtained [23].

The simplest model which explains the most intense δ peaks of Fig. 2 is represented in Fig. 3. This model implies the fullerene-induced reconstruction is accompanied by a very important mass redistribution within the unit cell since all compact atomic rows along the A_1 direction in the second layer have missing atoms. Moreover, the peaks in the δ map assigned to atoms in the topmost layer are 30% weaker than those corresponding to atoms placed immediately below them. This difference probably means that the topmost Au atoms are affected by positional disorder due to their low atomic coordination.

The rather weak intensity of the other peaks in the δ map implies that the deviations from the ideal positions of Au atoms in deeper layers must be very small and therefore excludes the participation of additional well ordered atoms in the $C_{60}/Au(110)$-$p(6 \times 5)$ reconstruction. Furthermore, the presence of highly disordered extra atoms in the topmost layers cannot be completely excluded since such atoms cannot be detected in the δ map. The $Au(110)$-(1×5) reconstruction observed by STM on adsorbate-free regions of the surface could be considered a precursor for the $p(6 \times 5)$ structure. This idea
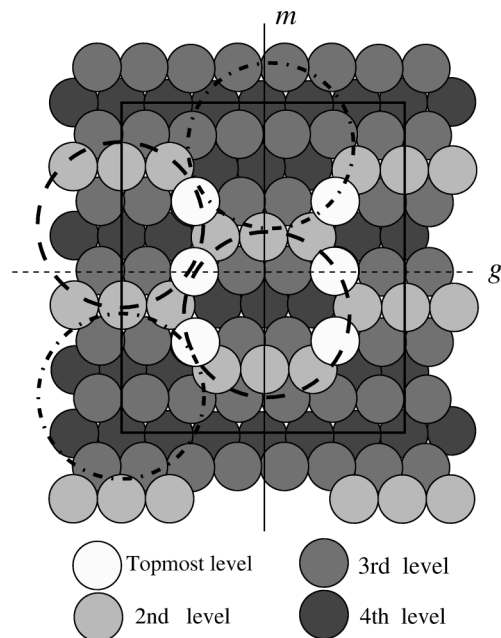

FIG. 3. Top view projection of the $C_{60}/Au(110)$-$p(6 \times 5)$ surface reconstruction. The relative heights of the Au atoms are indicated by different colors (darker shades represent deeper atoms). The fullerenes are indicated by the dashed circles. Two different dash styles have been used to make more clear the difference in heights of the molecules. Lines m and g indicate a mirror and a glide plane, respectively.

is supported by the fact that (a) its presence on the surface is not negligible and (b) the distances between the lines indicated by A, B, and A' in Fig. 2 coincide with those defining (1×2) and (1×3) ridges in the (1×5) reconstruction.

Let us now go back to Fig. 1 for a comparison between the observed data and those which can be calculated from the model of Fig. 3. The $p(6 \times 5)$ model proposed here has all the Au atoms in bulk crystal lattice positions and was refined with standard crystallographic procedures using the 108 in-plane data to a reduced $\chi^2 = 3.5$ (eight structural fit parameters, a global temperature factor B for the topmost layer, and one scaling factor). The maximum rms deviation of the fitted coordinates from the ideal values is 0.2 Å. The global B-value of the topmost atoms was refined to 5 Å^2 which is a relatively large value (about 5 times larger than that of the bulk atoms; see Ref. [15]). In spite of the limited number of refined variables, the agreement is rather remarkable as one can see from Fig. 1 where the filled semicircles are proportional to the structure factor amplitudes calculated with the proposed model. The calculation ignored the fullerenes since their scattering factor is very weak compared to the Au atoms, because of their relatively low electronic density. If the fullerenes are included in the structural model, the quality of the fit slightly improves.

In conclusion the $C_{60}/Au(110)$-$p(6 \times 5)$ system has been studied by x-ray diffraction measurements. Because of the large number of atoms in the unit cell standard crystallography procedures based on aprioristic models are inappropriate. We employed instead the 2D direct methods approach. The proposed structure implies corrugation of the C_{60} overlayer in agreement with STM results and reveals that the C_{60} adsorption is accompanied by important displacements of underlying Au atoms, leading to a calyx-shaped arrangement to accommodate better the fullerene molecules situated at $(0,0.6)$ and $(\frac{1}{2}, 0.4)$. The C_{60} molecules at $(0,0.1)$ and $(\frac{1}{2}, 0.9)$ have more space and rest directly on the low level Au atoms. Accordingly, the adsorbate overlayer is composed of zigzag and buckled rows since the fullerenes located at $(\frac{1}{2}, 0.4)$ and $(0,0.6)$ are expected to be one Au atomic level higher than the ones at $(0,0.1)$ and $(\frac{1}{2}, 0.9)$. The intermolecular distance between two fullerene molecules is about 10 Å, a value identical to the bulk C_{60}-C_{60} distance of 10.04 Å [24].

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