7 × 7 Reconstruction on Si(111) Resolved in Real Space

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The 7×7 reconstruction on Si(111) was observed in real space by scanning tunneling microscopy. The experiment strongly favors a modified adatom model with 12 adatoms per unit cell and an inhomogeneously relaxed underlying top layer.

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The 7×7 reconstruction of the Si(111) surface is one of the most intriguing problems in surface science. In recent years, most impressive experimental and theoretical efforts have dealt with the structure of this reconstruction.[1,2] However, the complexity of the large basic unit cell with 49 atoms is a serious handicap to deriving a structural model unambiguously even from an abundant set of experiments. Models in accordance with one class of experiments are in conflict with others.[1] The ever-increasing number of models and their variations appear to confuse rather than clarify the issue. In order to make significant progress, some basically new approach is required. Such a new approach is the *scanning tunneling microscopy* recently introduced by the authors.[3]

In the following, we report on the first *real-space* determination of the Si(111) 7×7 reconstruction. The scanning tunneling micrographs yield the principal structural features of the 7×7 unit cell.

The principle of the scanning tunneling microscope (STM) is explained in Ref. 3. It consists essentially in scanning a metal tip at constant tunnel current over the surface to be investigated. The corrugation monitored by the vertical motion of the tunnel tip reflects qualitatively the topography of the surface.

The 7×7 reconstruction was generated as follows. After etching the oxide with an HF solution the Si wafer was immediately transferred to the STM in the UHV chamber. Repeated heating to 900 °C in a vacuum not exceeding 3×10^{-8} Pa effects sublimation of the SiO layer grown during the transfer. This procedure is known to give fairly clean surfaces,[4] e.g., less than $\frac{1}{25}$ of a monolayer of carbon. However, the condition of the surface could not yet be tested by another contamination-sensitive method.

The micrographs were taken at 2.9 V (tip positive) since tunnel voltages below 2.5 V lead to direct contact between tip and sample. The voltage drop across the vacuum gap is smaller by an unknown amount because of band bending in the semiconductor. Only unidirectional scans (3 deg off the [$\bar{2}$11] direction) were recorded to avoid small but noticeable hysteresis effects of the scanning piezodrives.

The original recordings of two complete 7×7 unit cells are presented in Fig. 1 in relief form. The rhombohedral 7×7 unit cell is clearly bounded by the lines of minima with deep corners. Inside each cell, twelve maxima appear. The diagonals are 46 ± 1 and 29 ± 4 Å, in agreement with the crystallographic values of 46.56 and 26.88 Å, respectively. The short diagonal is less accurately determined since thermal drifts are more noticeable (scanning along the long diagonal with 2 sec/scan). For comparison with models, the cell size is adjusted to its proper value. Figure 2, a top view of Fig. 1, shows the sixfold rotational symmetry of the positions of the maxima around each corner. The minima pattern, however, ap-

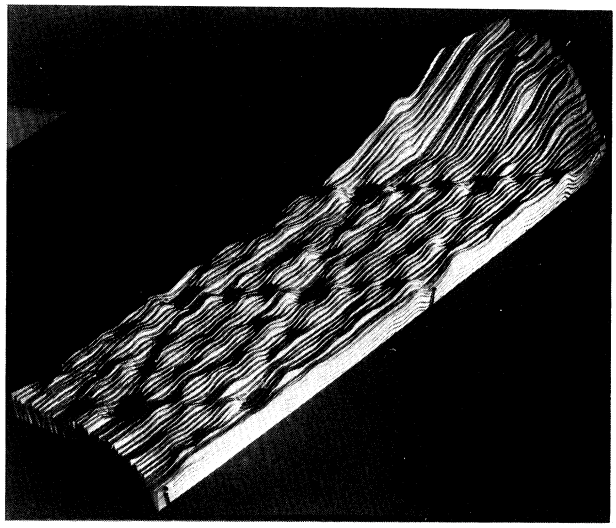

FIG. 1. Relief of two complete 7×7 unit cells, with nine minima and twelve maxima each, taken at 300 °C. Heights are enhanced by 55%; the hill at the right grows to a maximal height of 15 Å. The [$\bar{2}$11] direction points from right to left, along the long diagonal.

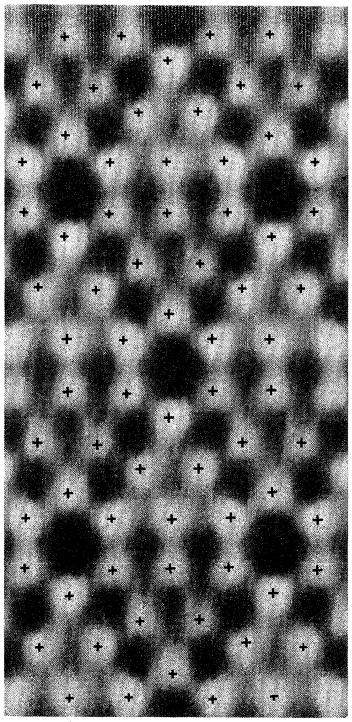

FIG. 2. Top view of the relief shown in Fig. 1 (the hill at the right is not included) clearly exhibiting the sixfold rotational symmetry of the maxima around the rhombohedron corners. Brightness is a measure of the altitude, but is not to scale. The crosses indicate adatom positions of the modified adatom model (see Fig. 3) or "milk-stool" positions (Ref. 5).

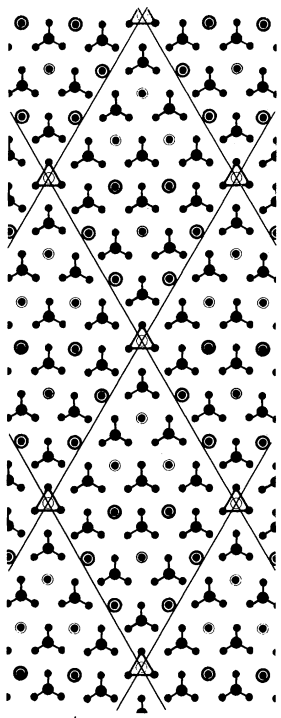

FIG. 3. Modified adatom model. The underlying top-layer atom positions are shown by dots, and the rest atoms with unsatisfied dangling bonds carry circles, whose thickness indicates the depth measured as discussed in the text. The adatoms are represented by large dots with corresponding bonding arms. The empty potential adatom position is indicated by an empty circle in the triangle of adjacent rest atoms. The grid indicates the 7×7 unit cells.

pears to have no rotational symmetry since it is deeper (on the average -0.26 Å) along the edges than along the short diagonal. A somewhat smaller height difference in the maxima is visually not as clearly evident in Fig. 2. However, we believe that these differences are experimental artifacts due to a slight overshoot when recording a minimum after a maximum (or vice versa). If we make the appropriate small corrections for this overshoot, the height of the maxima is uniformly 0.7 ± 0.1 Å with respect to an average level of zero for the unit cell. Likewise, the depth of the corner minimum becomes 2.1 ± 0.2 Å, and those along the edges and the short diagonal, 0.9 ± 0.1 Å. The depth of the single minimum in the left half of the cell is estimated at 0.5 ± 0.2 Å. Finally, a very shallow minimum with three arms of depth nearly zero lies in the right half of the cell. Then, the corrected minima pattern shows threefold rotational symmetry.

The maxima pattern is congruent with the positions of the "milk stools" in the model of Snyder, Wassermann, and Moskowitz[5] or with those of adatoms of a slight modification (missing adatom at the cell corner) of Harrison's model[6] (see Fig. 2). In both models, 36 dangling bonds of the truncated bulk surface are saturated by the adatoms or milk-stool atoms, leaving 13 (rest atoms) with unsatisfied bonds. The virtue of the milk-stool model is dangling bonds on neighboring sites (an important element also in the π-bonding model of Pandey[7]), and that of the adatom model, the reduction of dangling bonds. Our modified adatom model is shown in Fig. 3. In the milk-stool model, the adatom is replaced by a three-membered ring of atoms. Since tunneling is expected to occur predominantly from the dangling bonds, the maxima observed should reflect the dangling-bond positions of the topmost atoms. Then, the milk-stool model can hardly be reconciled with the experiment, since either 36 single maxima or a substantially different structure (e.g., a "doughnut" around the corner instead of six distinct maxima) should be observed, depending on

resolution.

In Fig. 4, we compare the lateral positions of the minima with those of the rest atoms of Fig. 3. The two patterns are again congruent within the experimental uncertainty of ± 0.5 Å when the three adjacent rest atoms are assigned to the deep corner minimum, and the three central rest atoms in the right half of the cell to the shallow three-armed minimum. In the model of Fig. 3, the adatoms sit on top of an "empty" triangular surface site (no atom below the adatom in the second layer). Shifting the adatoms to "filled" triangular surface sites (with an atom below the adatom in the second layer) corresponds to a reflection about the short diagonal. In that case, rest-atom sites and minima clearly do not match. Thus, the experiment unambiguously confirms the "empty" positions expected for the adatoms. Note also that the proposed milk-stool positions[5] correspond to "filled" sites.

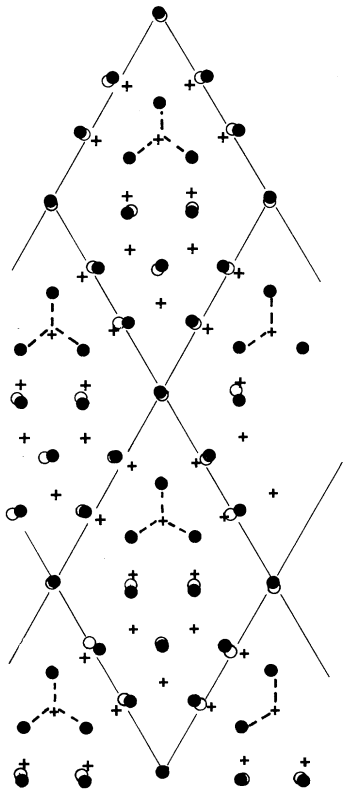

FIG. 4. Comparison of the lateral position of the minima (open circles, and three-armed star for the shallow minimum) with the rest-atom positions (filled circles for model of Fig. 3, crosses for reflection about the short diagonal). The diameter of the circles corresponds to 1.4 Å. The grid indicates the 7×7 unit cells.

The excellent agreement of the lateral positions of maxima and minima with those of the adatoms at "empty" sites, and of rest atoms, respectively, strongly supports, of the models already proposed, a slight modification of the adatom model[6] for the structure of the 7×7 unit cell. Of course, many interesting questions still remain open, two of which we briefly address below.

The first remark concerns the different depths of the minima. The deep and inhomogeneous corrugation observed cannot be explained by an unrelaxed adatom model. Nonuniform relaxation can, however, enhance the corrugation in a twofold manner: by the shift of the core positions and by relative changes of the energy of the dangling-bond states and/or their occupation. An appreciable tunneling corrugation by a change in bond occupation would require substantial charge transfer costing too much energy.[7] On the other hand, lowering the bond energy would substantially decrease the tunneling current through the shorter decay length into the vacuum gap. When shifted below the Fermi level of the counterelectrode, the state no longer even contributes to the tunnel current. A quantitative interpretation of the tunneling corrugation amplitudes found requires, however, a microscopic tunneling theory, which is still lacking.

A second point concerns the origin of the 7×7 structure. The adatom model with the lowest dangling-bond density is a $\sqrt{3}\times\sqrt{3}$ structure with no rest atoms. It appears that rest atoms are needed to provide (by inward relaxation) the charge transfer to the adatoms. However, if it were merely a matter of charge compensation, then a 2×2 reconstruction with equal number of adatoms and rest atoms would be most appealing. Therefore, we believe that the secret lies in the special nature of the corner, although other unit cells can be imagined with this key site. The smallest two, a $2\sqrt{3}\times 2\sqrt{3}$ and a 3×3, consist only of such key sites and have never been observed. The 5×5, also containing other sites, however, has been reported.[8] The unique character of the corner is not merely a matter of the three adjacent rest atoms. It is also the vertex of different kinds of regions. The 7×7 unit cell can be viewed as being composed of two equilateral triangles. The right one (see Fig. 3) contains practically unrelaxed rest atoms; in the other one the rest atoms are relaxed. These two kinds of triangles meet alternately at each corner. Preference for the 7×7 structure is likely the result of optimal balance of charge transfer and

stress.

In spite of the various interesting open questions, we trust that this Letter has clarified the basic aspects of a very intriguing problem, and will contribute to a better understanding of Si surfaces.

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Electronic and Magnetic Properties of Europium-Intercalated Graphite

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Stage-1 Eu-intercalated graphite EuC_6 was studied by Mössbauer and L-edge spectroscopy. Isomer shift and L_{III}-edge position results indicate the divalent state for Eu. Below 40 K, EuC_6 orders antiferromagnetically with the Eu spins oriented perpendicular to $\vec{c}$ and a magnetic hyperfine field saturating at -10.7 T. The large electric field gradient at the Eu site (-1.4×10^{18} V/cm^2), with axis parallel to $\vec{c}$, is consistent with the structure of EuC_6 and a partial charge transfer from Eu to the C planes.

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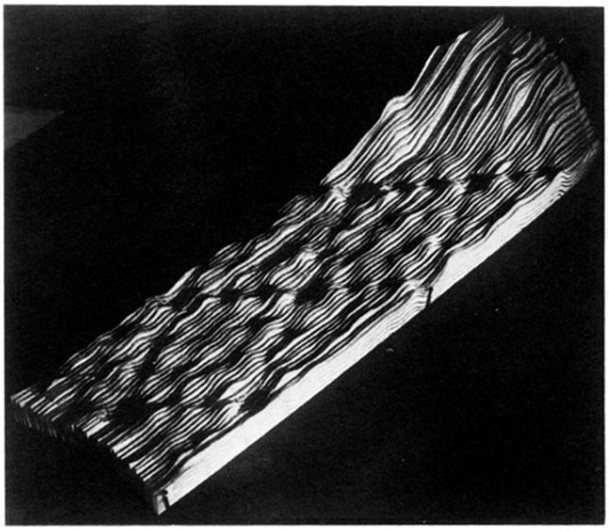
The highly anisotropic magnetic properties of graphite intercalation compounds (GIC) are of considerable current interest.[1,2] By increasing the number of graphite layers separating the two-dimensional arrays of magnetic intercalants studies of the transition from three-dimensional to more and more two-dimensional magnetic behavior are feasible.[3] Most of the relevant work so far has dealt with transition-metal chlorides as magnetic intercalants, and substantial changes in the magnetic properties relative to those of the pure intercalants were observed.[1-3] With the demonstration of the feasibility of vapor-phase intercalation of Eu,[4] a magnetic intercalation system with bare magnetic ions became available, since Eu is expected to intercalate in its $4f^7$-divalent magnetic state.[5] Higher-stage Eu GIC's should constitute prototypes for two-dimensional arrays of magnetic ions with almost isotropic exchange. Up to now only the results of magnetization measurements[5] and Raman studies[6] have been published for EuC_6.

The present paper reports on a ^{151}Eu Mössbauer study of EuC_6 as well as on L-edge x-ray absorption and magnetic measurements. From the observed Mössbauer isomer shift and the position of the L_{III} edge Eu is shown to be intercalated in its divalent state. The magnitude, negative sign, and orientation of the axially symmetric electric-field gradient (EFG) tensor at the Eu site are in quantitative agreement with the crystallographic structure of EuC_6.[4] Below 40 K the Mössbauer



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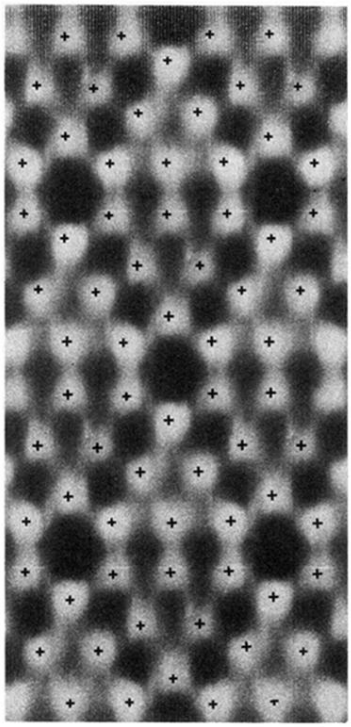

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