Direct Determination of the Au(110) Reconstructed Surface by X-Ray Diffraction

I. K. Robinson

Bell Laboratories, Murray Hill, New Jersey 07974

The method of glancing-incidence x-ray diffraction has been applied to the Au(110) reconstructed surface. The long-range structure is incommensurate with the bulk in one direction, comprising locally 2×1 regions separated by domain walls. The atomic positions in the 2×1 cell are determined independently of any models, and their alignment with respect to the bulk is deduced; the result is a missing-row structure with lateral pairing displacements in the second layer of 0.122 ± 0.017 Å.

A limited number of the elements show reconstruction of their surfaces. Exactly how a lowering of the symmetry can result in a reduction of the free energy is a question of fundamental interest that demands accurate structural information. This has been provided for some systems by low-energy electron diffraction (LEED) but not always without ambiguity[1,2] and never without elaborate model-dependent calculations.[3] The use of x-ray diffraction data in testing models of surface reconstruction[4] and in probing surface long-range order[5] has already been demonstrated, but its power in direct structure determination has not. That is the purpose of this Letter.

The (110)-terminated fcc structure consists of atoms in close-packed rows along surface [011] directions spaced apart by one unit cell ($a_0 = 4.08$ Å for Au) along the perpendicular [100] direction. Several models have been proposed for the observed 2×1 reconstruction of Au(110) to explain the doubling of the unit cell in the [100] direction. Most experimental evidence favors the class of "missing-row" models in which every second row of top-layer atoms is omitted[1,6-8] but "paired-row" and "buckled" models with alternating top-layer row displacements (parallel or perpendicular to the surface) are still considered possible.[8] Some analyses claim that an inward contraction of the top-layer spacing accompanies the reconstruction[1,6,7]; others suggest that it is intrinsically disordered[9] or decorated with adatoms.[10] We use here a Patterson synthesis of the x-ray diffraction intensities to derive the structure of Au(110) directly. It is of the missing-row type with *lateral* second-layer displacements and an expansion of the top-layer spacing. In addition, we are led to believe that the undulations seen along [100] in tunneling-microscope images[11] are associated with a slight incommensurability of the surface.

X-ray measurements were made on two differ-

ent single crystals of gold. Sample I was cut with the surface inclined 1.5° from [100] and was electropolished. Sample II was cut 0.1° from [100] and was mechanically polished. Both samples were cleaned in ultrahigh vacuum by repeated cycles of argon-ion bombardment and annealing at 350 °C over a period of several days until a sharp LEED pattern was obtained. Once prepared, this surface was stable for more than one week at 10^{-9} Torr and room temperature. The sample was transferred in UHV to a small chamber with beryllium windows[12] mounted on a four-circle diffractometer. X rays from a 30-kW rotating-anode source ($\lambda = 1.54$ Å) were focused onto the sample with a curved pyrolytic graphite monochromator and detected via a graphite analyzer. The sample was oriented with the crystallographic $(01\bar{1})$ plane lying in the horizontal diffraction plane of the instrument and aligned by means of the Bragg reflections therein. Because the crystal was imperfectly cut, the physical surface plane was not exactly coincident, and it was always possible to reach one of the symmetry equivalents of each reflection through the face of the crystal. Thus the incident and reflected rays made small angles with the surface. Conventional in-plane scans (Fig. 1) were made, as well as scans perpendicular to the diffraction plane by tilting the sample to track the continuous "rod" profiles arising from the surface (Fig. 2).

The most striking feature in Fig. 1 is that the half-order superlattice peak expected at $\frac{3}{2}00$ for a 2×1 reconstruction is actually displaced slightly. This immediately suggests that the surface is reconstructed in a way that has a long-range periodicity incommensurate with the bulk. The magnitude of the incommensurability, δ (defined as the peak displacement), varies with sample preparation as shown, but its direction is always along the surface [100]. The peaks are also broader than the instrumental resolution in this
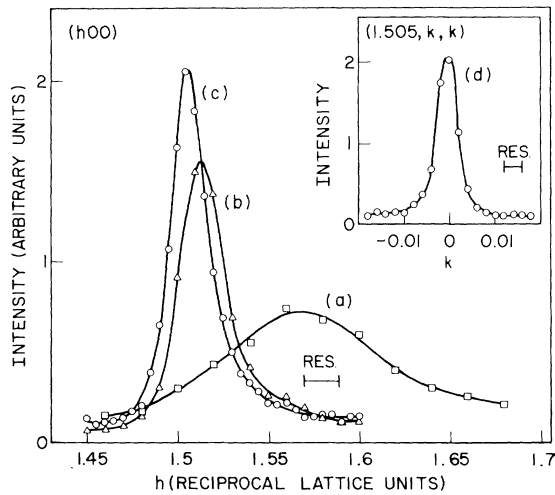
FIG. 1. X-ray diffractometer scans of the superlattice peak near $\frac{3}{2}00$. (a)—(c) Radial scans along [100], resolution (full width at half maximum) indicated. (a) Sample I, maximum counting rate 0.6 count/s. (b) Sample II, first preparation, maximum counting rate 2 counts/s. (c) Sample II, second preparation, maximum counting rate 10 counts/s. (d) Transverse scan, parallel to [011], of the peak in (c).

direction, with the width scaling roughly in proportion to δ. Along [011] the peaks are both sharp and perfectly aligned with the bulk, indicating a well ordered surface in this direction [Fig. 1(d)].

In order to understand the nature of the incommensurability, other superlattice reflections were measured. No higher-order multiples of the primary reflection at $(\frac{1}{2} - \delta, 0, 0)$ were seen, where $\delta = 0.006$ to 0.07 for the different samples; instead, superlattice peaks were seen at positions displaced by *bulk* reciprocal-lattice vectors from this primary location. This pattern is best described by an overlayer that is *locally* a 2×1 reconstruction of the bulk, interrupted by domain walls at regular intervals along [100]. A continuously incommensurate structure with a local misfit of spacings would give strong multiples of the primary peak and only weak satellites at bulk-shifted positions due to modulation.[13] A likely candidate for the domain wall is a monatomic step [(111) facet] in the surface, which produces a $\frac{1}{2}a_0$ phase shift between adjacent domains, that leads to the peak asymmetry. Statistical fluctuations in the step spacing give rise to broadened diffraction profiles in exactly the way that is observed. The average step spacing is then 170 Å for the $\delta = 0.006$ sample and 13 Å for $\delta = 0.07$; these values are much smaller than the *intrinsic*
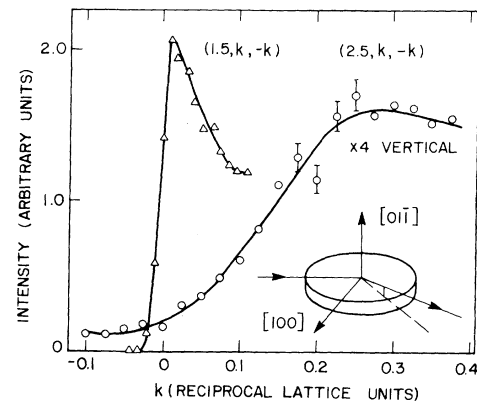

FIG. 2. Rod profiles parallel to [01$\bar{1}$] of two superlattice reflections performed at constant (glancing) incidence angle. The profile has intensity above the surface only; the resolution-limited edge at $k = 0$ corresponds to eclipsing of the exit beam by the sample.

step spacings (800 and 55 Å, respectively) arising from miscut of the crystals. We conclude, therefore, that steps (microfacets) form spontaneously under these preparation conditions.

Information about the *local* structure (between the domain walls) can be obtained by ignoring the displacements of the superlattice peaks and considering their intensity to correspond to structure factors at the exact half-order positions; these values are listed in Table I. Intensities were sampled along the rod profile (as in Fig. 2) and integrated in the [100] and [011] directions [Figs. 1(a) and 1(d)]. Only a polarization correction was applied as extinction effects should be

TABLE I. Observed structure factors (arbitrary scale) and the best calculated values for the three-parameter atom model described in the text. The R factor is 9%.

h	k	l	F_{obs}	F_{calc}
0.5	0	0	9.1	8.7
1.5	0	0	15.3	15.0
2.5	0	0	0	0.7
3.5	0	0	11.7	12.0
0.5	1	1	11.5	11.4
1.5	1	1	3.7	3.7
2.5	1	1	12.8	12.7
3.5	1	1	0	1.1
4.5	1	1	8.7	9.7
1.5	2	2	8.3	9.8
2.5	2	2	0	0.5
3.5	2	2	11.3	9.0

absent. The largest source of error is believed
to be variations in the diffraction geometry from
one reflection to another arising from misalign-
ment and miscut of the crystal; the measurement
procedure used reduced these errors to about 10%
in intensity, as determined from certain sym-
metry equivalent reflections.

The crystallographic tool most suitable to ana-
lyze these measurements in a model-independent
way is the Patterson (pair correlation) function,[14]

$$P(x,y,z) = \sum_{hkl} |F_{hkl}|^2 \cos 2\pi(hx + ky + lz).$$

This was calculated for the observed in-plane
reflections (F_{hkk}), to give the projection onto the
surface plane shown in Fig. 3. Since just frac-
tional-order reflections are included in this Fou-
rier synthesis, its features correspond to the re-
constructed region of the crystal only, involving
atoms in unique positions in the superlattice unit
cell and not repeated with the bulk spacing. The
presence of a large nonorigin peak in the Patter-
son at (0.6,0.25,0.25) identifies a single inter-
atomic vector that could reasonably describe a
structure with either two or three atoms per su-
perlattice unit cell; a minor peak at twice the
primary vector (0.8,0,0) favors three atoms.
Least-squares refinement of three atoms at
(0,0,0), $(x,0.25,0.25)$, $(-x,0.25,0.25)$, an over-
all temperature factor, B, and a scale factor
against the twelve observations gave the values
$x = 0.530 \pm 0.004$ and $B = 1.4 \pm 0.5$ Å^2 with an R fac-

tor,

$$R = \frac{\sum_i ||F_{obs}| - |F_{calc}||}{\sum_i |F_{obs}|} = 9\%,$$

which is entirely accounted for by errors of
measurement. The temperature factor corre-
sponds to an rms thermal vibration amplitude
(one component) of 0.13 ± 0.03 Å compared with
the bulk value of 0.084 Å at the same temperature
(293 K). Refinement of the most general two-
atom model gave an R factor of 14% which is con-
sidered unsatisfactory.

The arrangement of atoms in the 2×1 unit is
shown in projection in Fig. 3. Atoms A and B are
too close together (2.60 Å) to be coplanar with the
surface and so must belong to different layers.
Information about this third coordinate of the
atomic positions can be obtained from the rod pro-
files of Fig. 2, particularly those of the (2.5,0,0)
reflection shown and others that have an almost
vanishing structure factor in the hkk plane. The
mere fact that the rod profiles are not flat indi-
cates that the reconstruction involves more than
one layer. Six rod profiles were least-squares
fitted ($R = 12\%$) by the three-atom model with an
AB layer spacing of 2.06 ± 0.44 Å, under the as-
sumption that the two B atoms are coplanar with
the surface (relaxing this constraint did not lead
to a better fit). This represents a $40 \pm 30\%$ expan-
sion of the top-layer spacing.

The registry of this 2×1 overlayer unit cell
with respect to the bulk is not derivable from any
of these measurements, and so must be deduced.
In order to retain the full $2m$ symmetry of the
(110)-terminated bulk, the overlayer A atoms
must lie upon one of the four (independent) two-
fold axes of the bulk unit cell; since either the A
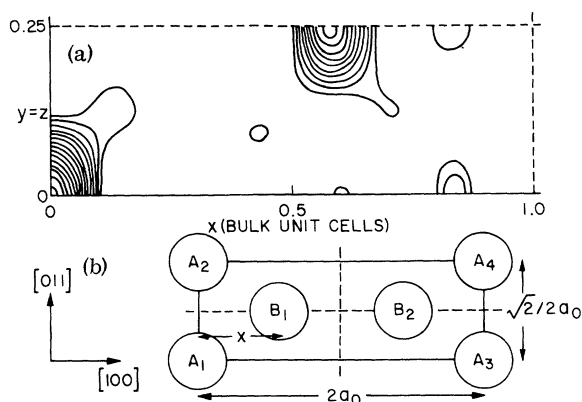layer or B layer could be topmost, there are

FIG. 3. (a) Contour map of the hkk projection of the
Patterson function. Only positive contour levels above
the first are shown. The asymmetric unit is $\frac{1}{4}$ of the
2×1 unit cell, as indicated by the two mirror planes;
$2m$ symmetry has been assumed. (b) Interpretation of
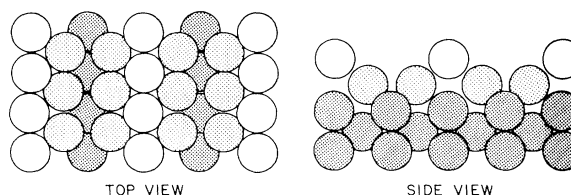the atomic positions in the full 2×1 unit cell.

FIG. 4. Full three-dimensional model of the local
structure of Au(110). The atomic displacements have
been exaggerated for clarity. The lateral displace-
ments in the second layer (light shading) are 0.122
± 0.017 Å. The top layer (unshaded) is 2.06 ± 0.44 Å
above the second. Atoms in bulk positions are heavily
shaded.

eight possible structures. Of these, the one that offers by far the highest average coordination has the A atoms on top and the B atoms as the second layer, displaced laterally from their bulk positions by 0.122 ± 0.17 Å. This structure, shown in Fig. 4, is the missing-row model with second-layer pairing. The "paired-row," "buckled," and "sawtooth"[10] models all involve an even number of atoms in the 2×1 unit cell and are therefore excluded.

In conclusion, we agree with the consensus of previous experimental results that the *local* structure of Au(110) is of the missing-row type. We find a second-layer pairing that has not been observed before. We also see an expansion of the top-layer spacing that contradicts the 15% contraction deduced from analysis of the LEED results, and the 10% contraction from analysis of He diffraction data.[6] It is interesting to note that the LEED analysis of the related 2×1 Pt(110) surface has two solutions for the missing-row model, the first a 23% expansion and the second a 20% contraction,[15] and that positive values of the layer-spacing shift were not considered in the original Au(110) analysis.[1]

The long-range structure is slightly incommensurate along [100] with an array of domain walls that are probably steps in the surface. The spacing of these varies with preparation conditions in the range 13–170 Å that is completely consistent with the 100-Å-period undulations seen along [100] in tunneling microscope observations.[11] Our experimental results agree with previous LEED line-shape measurements showing broadening along [100],[9] but we disagree with the conclusion of a disordered surface.

I would like to thank W. Toy for preparing one

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