

X-ray standing-wave determination of surface structure: Au on Si(111)

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The structure of Au submonolayers on Si(111) has been investigated as a function of annealing using x-ray standing waves. Au L_{III} photoelectron yields reveal that the Au sites are embedded in the topmost Si(111) planes, the precise position being dependent on the extent of annealing. Standing-wave yields of the Si L_{VV} and KLL Auger electrons were also measured, before and after Au deposition. These results show that the initially contracted Si surface relaxes outwards along with the embedded Au atoms with continued incorporation of Au into the surface.

The effort to determine the structure of crystal surfaces and the causes of surface reconstruction has led to the development of a large number of structural probes. Historically, low-energy electron diffraction (LEED) has been the most productive technique for establishing the dimensions of the surface unit mesh, but multiple-scattering effects make the determination of atom locations very difficult. Other surface structural probes which can supplement the LEED results include ion-scattering spectroscopies, surface extended x-ray-absorption fine structure, surface x-ray diffraction, transmission electron microscopy, and, the most recent, scanning tunneling microscopy. As yet, no single method can provide a complete picture of surface structure. In addition, there is still a significant degree of uncertainty in the structure of those surfaces which have been investigated by nearly all available techniques, e.g., the 7×7 reconstruction of Si(111) surfaces.^{1,2}

We report here the extension of the x-ray standing-wave technique to the study of surfaces in ultrahigh vacuum. The structural information obtained is complementary to that derived from other surface probes, and in favorable cases can determine surface atom positions with considerably greater accuracy than otherwise possible. The x-ray standing-wave technique has proven capable of determining impurity locations in nearly perfect crystals with an accuracy better than 1% of a lattice constant.³⁻⁷ It has also been successfully extended to the determination of surface adsorbate locations, most notably for Br on Si.⁸⁻¹⁰ In previously reported studies, however, the surfaces were typically examined in air instead of in the high vacuum normally required to keep a surface clean and well characterized. We describe below a standing-wave study of Au on the Si(111)¹¹⁻¹³ surface, measured in ultrahigh vacuum (UHV) with the capability of simultaneously monitoring the surface composition and structural order with Auger spectroscopy and LEED.

The interaction of x rays with perfect crystals, where the diffracted beams have intensities comparable to that of the incident beam, is described by the dynamical diffraction theory.¹⁴⁻¹⁶ The coupling between the electromagnetic radiation and the periodic dielectric function of the crystal results in the absence of propagating solutions of Maxwell's equations for scattering wave vectors in the vicinity of a reciprocal-lattice vector \mathbf{H} , where Bragg diffraction occurs. The incident x rays which correspond to these wave vectors

cannot excite traveling waves inside the crystal and are completely reflected (except for small losses due primarily to photoelectric absorption), resulting in the characteristic Darwin reflectivity curve.^{16,17}

The incident wave with wave vector \mathbf{k}_0 and a reflected wave with wave vector \mathbf{k} will interfere when $\mathbf{k} = \mathbf{k}_0 + \mathbf{H}$, where \mathbf{H} is a reciprocal-lattice vector, to produce a standing wave with stationary nodal planes normal to the \mathbf{H} direction and with a periodicity of $d_H = |\mathbf{H}|^{-1}$. (All x-ray wave vectors refer to their vacuum values.) For the Bragg-diffraction geometry, dynamical diffraction theory predicts that only one standing-wave solution with a unique phase will exist. Outside the region of total reflectivity, the phase of the standing wave for $|\mathbf{K}| < |\mathbf{H}|$ (where \mathbf{K} is the scattering wave vector, $\mathbf{K} = \mathbf{k} - \mathbf{k}_0$) is such that the nodes of the electric field intensity coincide with the diffraction planes, which are essentially the maxima of the \mathbf{H} Fourier component of the electron density; for $|\mathbf{K}| > |\mathbf{H}|$ the nodes fall midway between the diffraction planes. The standing-wave phase varies smoothly between these two positions for those wave vectors within the Darwin width.

The key to the use of the standing wave as a probe of atom positions is the proportionality between electric field intensity and photoelectric excitations. The resultant photoelectron yield and the yields from fluorescence and Auger electron deexcitation channels are then direct measures of the electric field intensity at the center of the atom.¹⁸ (Thermal and Compton scattering of the x rays also exhibit this dependence on electric field intensity.¹⁹) If, for example, a distribution of surface or impurity atoms has a fraction f occupying a specific type of site at a position Δd with respect to the diffraction planes (of spacing d_H), with the remaining fraction $1 - f$ randomly distributed, then the inelastic yield will be^{16,20}

$$Y = 1 + \left| \frac{\mathbf{E}_H}{\mathbf{E}_0} \right|^2 + 2P \left| \frac{\mathbf{E}_H}{\mathbf{E}_0} \right| f \exp(-2\pi^2 \langle u^2 \rangle / d_H^2) \times \cos \left(\phi - \frac{2\pi \Delta d}{d_H} \right), \quad (1)$$

where \mathbf{E}_0 and \mathbf{E}_H are the incident and reflected electric fields, ϕ is the standing-wave phase, P is the x-ray polarization factor, and $\langle u^2 \rangle$ is the mean-square vibrational amplitude.²⁰ Extinction is ignored here, because the experiments

to be described measure yields only from surface species.

The experiments were conducted at the Cornell High Energy Synchrotron Source (CHESS). The incident x-ray beam was monochromated and collimated to have an angular divergence smaller than the sample Darwin width by a new type of Si(111) channel-cut monochromator, which is described elsewhere.²¹ We examined polished Si(111) substrates maintained in a UHV chamber (base pressure $< 10^{-10}$ Torr), equipped with a cylindrical-mirror analyzer (CMA) for high-resolution electron spectroscopy and with LEED optics to observe surface ordering. The Si samples were cleaned by radiative heating to as high as 1100 °C until no impurities were detectable in the Auger spectra and a 7×7 reconstruction was seen with LEED. Submonolayer coverages of Au were deposited from a heated filament.

In previous standing-wave studies³⁻⁹ the monochromator typically was stationary and the sample was rotated through the Bragg reflection. Despite the interest in surfaces, standing-wave studies were not conducted in UHV because of the difficulties in controlling sample rotations with sub-arc-second precision using standard UHV equipment. This difficulty is surmounted by scanning the scattering wave vector

$$|\mathbf{K}| = (4\pi/\lambda) \sin\theta$$

by changing the monochromator angle, i.e., by changing λ ; this allowed the sample to remain fixed in the vacuum chamber.^{22,23}

To examine Au deposited on Si, the Au L_{III} photoelectrons were counted with the CMA. Because the Au photoelectron peak sits on a background of Auger and photoelectrons, the standing-wave scans were always repeated after reducing the x-ray energy enough to move the pho-

toelectron peak outside the fixed CMA energy window (band pass = 1.2%). These data were then subtracted from the original data, leaving the Au L_{III} photoelectron signal essentially free of background contributions. The experimental setup and a representative electron spectrum are shown in Fig. 1; representative reflectivity and standing-wave yield curves are shown in Fig. 2. About 50 Au L_{III} counts/sec were detected during typical standing-wave scans.

Note that all of the measurements reported here refer to positions in the surface normal direction only. The lateral registry of Au atoms can be determined from standing-wave measurements using off-normal Si Bragg reflections, but this was not feasible with the available equipment, largely because of strict limitations imposed on the diffraction geometry by the positions of the chamber x-ray ports and the CMA.

We present here the results of photoelectron standing-wave measurements on two Si(111) substrates with Au coverages of 0.3 and 0.4 monolayers²⁴ (one monolayer = 7.8×10^{14} atoms/cm²). Three sets of data were taken on each: (i) immediately after deposition onto a room-temperature substrate having an initial 7×7 reconstruction, (ii) after annealing at 300 °C to obtain a sharp 1×1 LEED pattern, and (iii) after annealing at 500 °C to obtain a 5×1 pattern.

Equation (1) was convoluted with the monochromator transmission function and fitted to the data shown in Fig. 3, using a least-squares technique. It was assumed that the distribution of Au atoms at the surface contained a fraction f located Δd from the (111) diffraction planes, with the remainder randomly distributed in the [111] direction. Because the standing wave is generated by diffraction from many planes extending far below the surface into the bulk crystal, this position is with respect to the perfect unreconstructed Si(111) planes, not to the actual top layer of Si

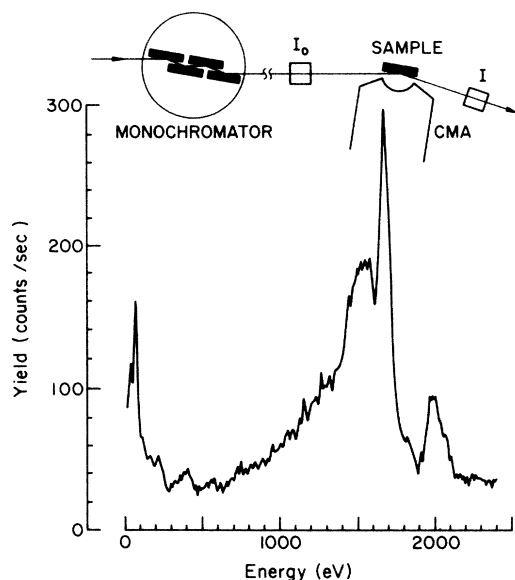


FIG. 1. Top: Schematic showing the incident synchrotron beam striking the monochromator, an ion chamber for monitoring the incident intensity (I_0), the sample set to diffract the monochromatic beam [while at the focus of a cylindrical-mirror electron analyzer (CMA)], and an ion chamber for detecting the diffracted intensity (I). The sample and the CMA are in a UHV chamber equipped with beryllium windows. Bottom: An electron spectrum recorded by the CMA with 13.6-keV x rays striking a surface of 0.4 ML of Au on Si(111). The peak near 1700 eV is due to Au L_{III} photoelectrons; other structures are various Au and Si Auger peaks.

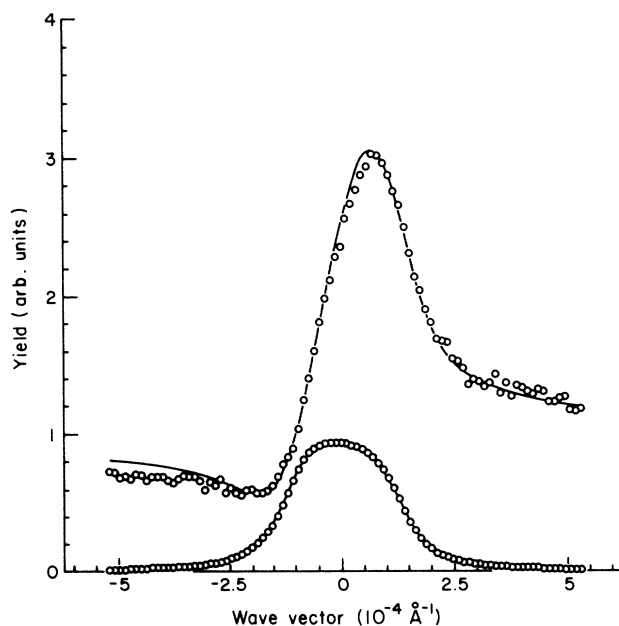


FIG. 2. The lower curve is the measured reflectivity of a Si(111) crystal (O) using 13.6-keV x rays. The upper curve shows the measured L_{III} photoelectron yield from an Au coverage of 0.3 ML (O), with the asymptotes normalized to unity. The fit to this curve was derived from Eq. (1).

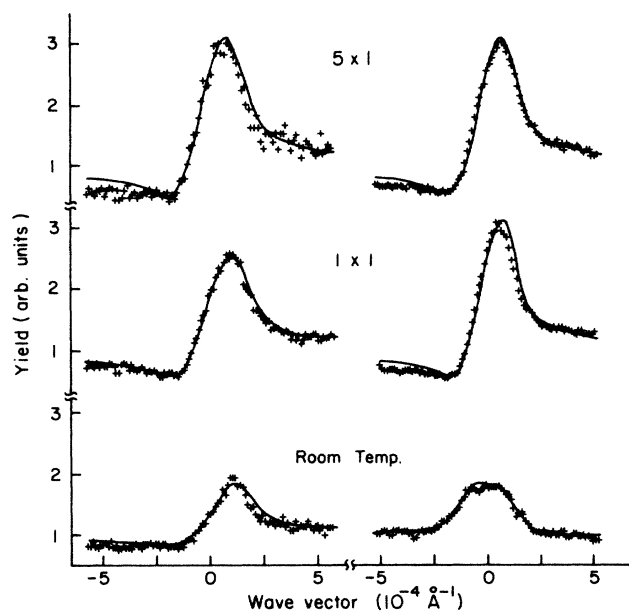


FIG. 3. Annealing study of the Au photoelectron standing-wave yield for coverages of 0.4 (left) and 0.3 (right) ML on Si(111). Lowest curves were obtained immediately after deposition onto room-temperature substrates, the middle curves were taken after annealing at about 300°C for 15 min, and the top curves resulted after a 15-min anneal at about 500°C. The first anneal produced a sharp 1×1 LEED pattern, which was converted to a 5×1 pattern by the second anneal.

atoms, which may be reconstructed. Results of the analysis are shown in Table I.

After room-temperature deposition of Au, the 7×7 Si(111) LEED patterns changed to patterns with very broad 1×1 spots with a strong diffuse background. Large differences were observed in the coherent fraction f and the relative coherent position or $\Delta d/d_{111}$ for the as-deposited surfaces with 0.3- and 0.4-ML (monolayers) Au coverage. Based on previous LEED and Auger studies,^{11,12} we find no reason to expect that this small change in coverage would have a large effect on the distribution of Au atoms. These differences may be the result of different initial surface conditions. Although both surfaces initially had 7×7 LEED patterns, the overall quality of the superlattice spots could vary depending on each sample's particular cleaning history. Other factors may include the Au source temperature, deposition rate, and substrate temperature. While these were nominally the same for both samples, a systematic study of these factors might reveal the origin of the differences.

The coherent fraction values of 8% and 57% show that even at room temperature some fraction of the Au adatoms

TABLE I. Values for the coherent fraction f and the relative coherent position (denoted by $\Delta d/d_{111}$) are presented for the data shown in Fig. 3 from two different Si(111) samples with Au coverages of 0.3 and 0.4 ML.

Au phase	0.3 ML Au		0.4 ML Au	
	$\Delta d/d_{111}$	f	$\Delta d/d_{111}$	f
As deposited	-0.30	8%	-0.11	57%
Annealed, 1×1	+0.06	90%	-0.01	80%
Annealed, 5×1	+0.06	93%	+0.06	98%

have sufficient mobility to find the preferred bonding site. As can be seen from Eq. (1), however, a small value of f leads to greater uncertainty in determining $\Delta d/d_{111}$. The coherent positions for these two surfaces ($\Delta d/d_{111}$ values of -0.30 and -0.11) should perhaps be considered as semi-quantitative. Even so, these positions are significantly below the top Si ideal plane position at +0.125; in fact, they are in the vicinity of the ideal second-layer position at -0.125. (An illustration of the ideal Si structure is presented in Fig. 4, inset.) This location of the Au atoms, which is contrary to the usual picture of adatoms residing on top of the substrate surface planes, implies that either the Au atoms are deeply embedded or that the Si surface planes are significantly contracted, or both.

Annealing the as-deposited surfaces at approximately 300°C for 15 min provided LEED patterns with sharp 1×1 spots. A dramatic increase in the coherent fraction to 90% and 80% for the samples with 0.3- and 0.4-ML Au coverage, respectively, indicates that the as-deposited Au atoms had small coherent fractions because of insufficient thermal energy to bond into the preferred sites.

The coherent position of the Au moved outward (to $\Delta d/d_{111} = +0.06$ and -0.01 for the two coverages, respectively) but is still well below the top unreconstructed plane position of +0.125. There is a consistent pattern in these and other measurements on similar samples, in that the Au coherent position moves out as the coherent fraction increases. This can be accounted for by assuming that the preferred Au site is embedded within the initially contracted top two Si planes, and that the physical overcrowding caused by increasing numbers of oversized Au atoms is relieved by

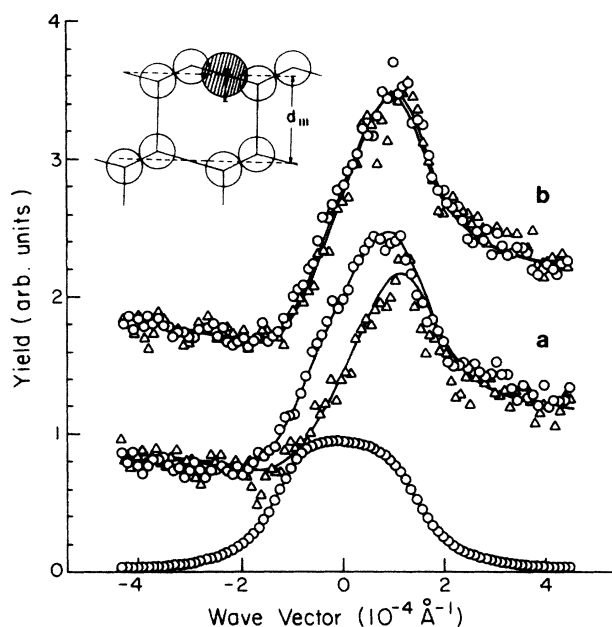


FIG. 4. Standing-wave yields are shown for the Si LVV (Δ) and KLL (O) Auger peaks; the lowest curve shows the x-ray reflectivity data. The lower set of LVV and KLL Auger yield curves (a) were collected from a clean, 7×7 reconstructed Si(111) surface. The difference in these LVV and KLL curves is attributed to a surface contraction of about 0.5 Å. The upper set of LVV and KLL curves (b) (displaced by one unit along the ordinate for clarity) were taken from a 5×1 Au on Si(111) surface, and indicate bulklike surface positions. Inset: Cross section of ideal Si(111) surface with Au in hollow site. Arrow shows range of Au positions noted in Table I.

the outward relaxation of the Si planes.

When the samples were annealed another 15 min at about 500°C, the LEED pattern revealed a 5×1 reconstructed surface, in agreement with the work of LeLay.^{11,12} The coherent fractions continue to approach 100%, but the coherent positions appear to have reached a terminal value of +0.06. Thus we find the initial differences in the as-deposited surfaces have disappeared upon formation of the 5×1 surface, with nearly all Au atoms now in identical sites. The large coherent fractions reduce the uncertainty in the deduced values of $\Delta d/d_{111}$. We find for the 5×1 data sets shown in Fig. 3 that the curves generated by changing $\Delta d/d_{111}$ by $\pm 2\%$ from the best-fit value lie outside the scatter in the data; we conclude that the uncertainty in $\Delta d/d_{111}$ is $\pm 1\%$.

This location of the Au atoms near the diffraction plane suggests that they reside in a surface hollow site between the top two Si atomic planes. A position precisely at the diffraction planes ($\Delta d/d_{111} = 0$) would correspond to the model proposed by Yabuuchi, Shoji, Oura, and Hanawa.¹³ Their ion-scattering measurements revealed that some Si atoms shadow the Au atoms, i.e., the Au atoms must be embedded, with the surface hollow site being the most plausible location. The standing-wave results confirm that the site is embedded, but with a position 6% above the diffraction plane. Based on the dependence of this position on the coherent fraction as described above, we infer that the top two Si planes relax outward from initially contracted positions in response to the Au incorporation.

The results in Table I are all derived from measurements of Au photoelectrons, so while the Au positions with respect to the ideal diffraction planes have been accurately determined, we have thus far only been able to speculate on the positions of the neighboring Si atoms. To obtain direct information, measurements were made of the Si *LVV* and *KLL* Auger electron standing-wave yields from 7×7 Si(111) and 5×1 Au on Si(111) surfaces; one set of these data is shown in Fig. 4. The analysis here is more complicated because much of the signal originates below the surface atoms, since the mean free path is $\approx 7 \text{ \AA}$ for the *LVV* and

$\approx 25 \text{ \AA}$ for the *KLL* Auger electrons. Changes in the surface structure are primarily revealed as differences in the *LVV* and *KLL* standing-wave curves, since the surface layers comprise a much larger fraction of the *LVV* signal.

The analysis of the clean 7×7 Si surface data reveals a significant contraction of the two top planes by $18 \pm 5\%$ of the (111) spacing, or about 0.5 Å; this result is presented in detail in another publication.²⁵ This conclusion follows directly from the clear separation of the *LVV* and *KLL* curves in Fig. 4(a). As shown in Fig. 4(b), however, this difference is no longer observable after the formation of the 5×1 Au overlayer, indicating that the top two Si atomic planes are now close to their ideal bulk positions. This represents direct confirmation of our earlier suggestion that the top Si planes are initially contracted by a significant amount, and that the outward motion of the Au coherent position is accompanied by a similar relaxation of the top Si planes.

We conclude that the 5×1 reconstructed Au on Si(111) surface consists of Au atoms situated at $\Delta d/d_{111} = +0.06$ above the bulk diffraction plane, between the two top Si planes which are relaxed from initially contracted positions. This embedded Au site is very different from the common chemisorption bonding sites on top of the substrate surface, such as the atop position deduced for Br⁹ and Al (Ref. 26) on Si(111). We note, however, that the bonding of Au to Si in which *d* electrons participate is quite different from the bonding of either Br or Al which primarily involves *s-p* electrons.²⁷

Finally, we believe that this study establishes the UHV x-ray standing-wave technique as a powerful surface probe, especially when combined with high-resolution electron spectroscopy and a synchrotron source.

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