

Stepped Silicon Templates for Quantum Wire Structures

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ABSTRACT

During the twenty-year development of synchrotron radiation sources for X-ray diffraction, the application to surfaces and interfaces has been a primary motive for the technological advances. The experimental techniques, which are now well-developed, are described in the introduction of this paper. A recent application has been to understand the quantum physics of one-dimensional electronic structures. Here a vicinal semiconducting surface, Si(557), is used as a template to grow ordered arrays of metallic wires by evaporation of gold. The structure of the resulting Au/Si(557) surface is determined from three-dimensional X-ray diffraction measurements. The data directly mandate a single Au atom per unit cell, which allows the use of a 'heavy atom' method in which the Au atom images the rest of the structure. Au is found to substitute for a row of first-layer Si atoms in the middle of the terrace, which then reconstructs by step rebonding and adatoms. This structure is found from theoretical band structure calculations to be consistent with the 1D metallic behavior seen by photoemission.

Surface X-ray Diffraction is a useful experimental method to learn about the atomic-scale structure of surfaces and interfaces. The well-known penetrating property of X-rays inside solid and liquid matter allows us to examine both surfaces and interfaces on an equal footing. Whereas an inherently surface-sensitive method like Scanning Tunnelling Microscopy (STM) can detect the outermost electron shells of the topmost layer, Surface X-ray Diffraction sees the full three-dimensional arrangement of the atom cores. Sometimes, the distinction is important, for example when the electronic density of states is under investigation. In the example presented here, Au/Si(557), the STM is ambiguous about the chemical identity of the prominent features and the electronic states are relevant to its functioning as a quantum wire.

It is commonly not appreciated that Surface X-ray Diffraction obtains its surface sensitivity from *symmetry* considerations alone. Because a surface has lower symmetry than the bulk, its diffraction extends out into regions of reciprocal space where the bulk does not contribute. By choosing to measure in those places, the experiment can be specific about surface structure. Apart from the trivial breaking of the translational symmetry in a reconstructed surface, which leads to entirely new diffraction features, even a "1x1" surface can be determined by Surface X-ray Diffraction because of its Crystal Truncation Rods (CTRs). The Au/Si(557) surface presented here is such an example.

Crystal Truncation Rods (CTRs) arise because of the abrupt termination of a semi-infinite crystal at a flat surface [1]. They were anticipated by von Laue in his calculation of the contribution of crystallite shapes to powder diffraction profiles [2]. While a mathematical derivation is provided in ref [1], CTRs can be understood graphically to be a convolution, as illustrated in Fig 1. The semi-infinite crystal is represented as a *product* of an infinite crystal with a step function cutting it off in the *z*-direction. According to the convolution theorem, the diffraction pattern is the *convolution* of the Fourier transforms of these two functions. The Fourier transform of an infinite lattice is a reciprocal lattice of ideal δ -function-like points, given by the usual construction. The Fourier transform of a step function in *z* is $1/q_z$, giving the $(1/q_z)^2$ functional form for the intensity illustrated in Fig 1. Upon convolution, the $(1/q_z)^2$ functions join together to form continuous lines through reciprocal space, whose intensity diverges at each Bragg point, as shown. In the real situation, absorption (or else dynamical effects) prevents this divergence of intensity. Usually, the surface is a close-packed crystal plane in real space; by the reciprocal lattice construction, the normal to this plane, spanned by q_z , is an exact direction of reciprocal space, along which the Bragg peaks line up.

Near to the Bragg peaks, the CTRs are sensitive only to the bulk structure, represented through the usual bulk structure factor. Far away, the CTRs become progressively more surface sensitive, both to the atomic structure and to the degree that roughness is present [1]. The Surface X-ray Diffraction method therefore consists of measuring the intensities of a large number of CTRs and comparing with the surface structure factor calculated as the amplitude sum of the surface and bulk. A widely used computer program, called ROD, allows the refinement of the atomic coordinates in three dimensions [3]. ROD is not useful for *ab initio* modelling because of the phase problem inherent to all X-ray Diffraction methods; a close starting model is required. Because of its simplicity, having a single heavy atom (Au) per unit cell, the Au/Si(557) structure "solves itself". As first shown for small molecules [4], the pair correlation (Patterson) function, obtained by Fourier transformation of the measured intensities, closely resembles the electron density of the structure combined with its inverted "twin" image.

The clean Si(557) surface was prepared on a wafer fragment by heating it in UHV to 1200°C. As previously reported [5], this resulted in a 3x1 reconstruction, believed to be comprised of triple bunches of steps. Part of its diffraction pattern is shown in Fig 2. The indexing of the reciprocal lattice appears unusual, but is required to meet the necessary condition of placing the q_z -direction along the (557) surface normal. The 11-1 bulk reflection indexes as (12,0,3), while the 220 bulk reflection indexes as (14,0,20) in these "surface" coordinates [6]. The (12,0,L) and (14,0,L) CTRs can be clearly seen as ridges of intensity in the contour plot, rising strongly towards the two Bragg peaks, just off the edge of the frame. Two additional rods of intensity lie in between the CTRs at 1/3-order positions, which are due to the reconstruction.

This (presumably) step-bunched substrate was then used as a template to prepare the Au/Si(557) surface by evaporation of 0.2 monolayers of Au onto the substrate at 600°C then annealing briefly at 900°C. The annealing permits the substrate atoms to rearrange, resulting in a "1x1" surface, containing only the (12,0,L) and (14,0,L) CTRs and no 1/3-order rods [6]. This is the structure we solved by measurement of the intensities of the CTRs [6]. The Patterson function gave us directly the termination of the Si lattice at the surface. Some additional peaks in the Patterson suggested small modifications, which were tested and refined using ROD to give the final structure of Fig 3.

In describing the final structure, the most noteworthy feature is that the Au atom substitutes for a row of Si atoms right in the *middle* of the terrace. The

substitutional behavior is new in the sense that all previous structures of Au on Si surfaces have been ambiguous about the binding site(s). Here it is very clear that almost ideal substitution takes place in the upper bilayer, resulting in Au-Si bondlengths of 2.46Å and 2.35Å, which are within the limits of error from Si-Si at 2.35Å; the Au appears to substitute in the Si lattice with relatively little strain. The second main feature is that the step edge reconstructs to form a 5-membered ring, but removes a dangling bond. The third feature is a row of adatoms attached to (otherwise) dangling bonds, as shown. The adatoms were only just detectable with the current number and quality of data (349 independent measurements, 47 structural parameters), reducing the chisquare from 7.5 to 7.1 for the final model.

The adatom row, which improved the fit to the X-ray data, can only be 50% occupied within our model, which assumes a single repeat of the bulk Si structure in the y-direction (see Fig 3). This is because it requires three upper bilayer dangling bonds on a Si(111) terrace to attach an adatom, so two unit cells along y are needed. In fitting the data, a 50% occupancy per single unit cell was therefore assumed. The finding of reduced occupancy might account for the doubled periodicity of one of the two rows seen per unit cell seen in the STM results, an example of which is compared with our model in Fig 4.

The main purpose of Fig 4 is to compare the relative distances along the x-direction between the protruding features of the model and STM image. The row spacing of the STM is unfortunately compatible with two possible spacings of the atomic model, so the identification remains ambiguous: the second row could be either the Au or the step edge. We identify this other row to be the step edge for two reasons. Firstly, the peaks of both rows appear alike in STM, even at different tunnelling voltages. Secondly, even though the step edge is not expected from our model to have a doubled period, it shows one nevertheless. Since the adatom is known to induce considerable strain parallel to the surface, it is conceivable that a buckling of the step-edge atoms could result. Such a buckling was already found to lower the surface energy in an *ab initio* calculation [7]. Conversely, buckling of an Au row is not supported. This prediction, which would explain the STM findings, is testable in a future X-ray diffraction experiment, if the surface can be ordered sufficiently to obtain half-order diffraction peaks along the y-direction.

Refined atomic coordinates are provided in Table 1. Crystallographic notation is used, giving coordinates as fractions of an orthorhombic unit cell that contains two copies of each atom. The numbering scheme is marked using labels in Fig 5. Fig 5 also denotes the bond lengths that are identified in the model. Excluding the

adatom, these were found to be distributed with an average of 2.37\AA and a standard deviation of 0.07\AA . The bulk Si bond length is 2.35\AA . The adatom geometry showed a back-bond length of $2.11 \pm 0.2\text{\AA}$, although this is a little unreliable because of its low occupancy. There is a significant trend in bond angles that affects the overall appearance of the surface in Fig 5. Close to the underside of the step, the geometry is close to tetrahedral near 109° , suggesting sp^3 bonding. This tends towards trigonal near 120° , indicating sp^2 bonding, at the outermost end of the terrace.

Ab initio calculations for the structure of Fig 2 have already been completed [7]. The calculation compared a number of possible configurations and independently found the same step reconstruction [7]. The adatom was found to be acceptable to the total energy, but without a strong difference. The middle Au substitutional site was also confirmed to be favorable and found to contribute to strongly hybridized Au-Si electron bands which cross the Fermi level. These are the states that contribute to the one-dimensional conductivity in this system.

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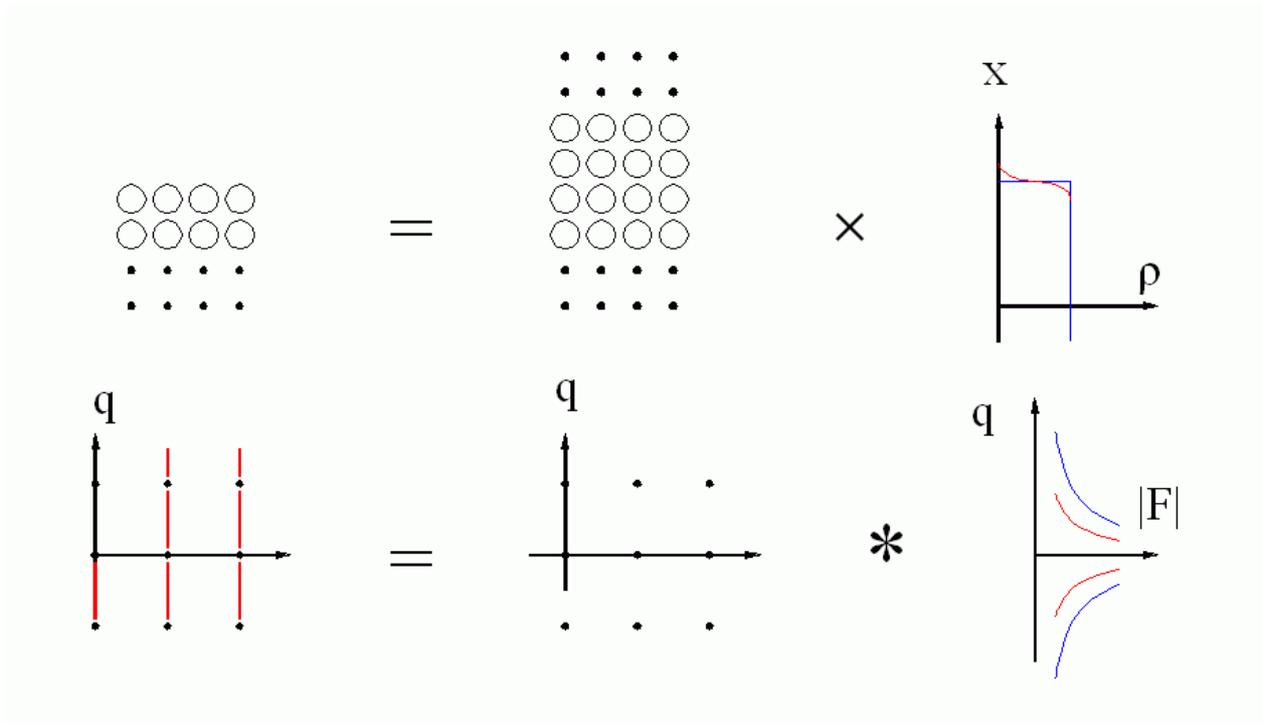


Figure 1. Pictorial view of the origin of Crystal Truncation Rods as a convolution. Top row: surface of a crystal is obtained by *multiplication* of an infinite crystal by a step function. Bottom row: after Fourier transformation, the diffraction pattern is obtained by the corresponding *convolution*.

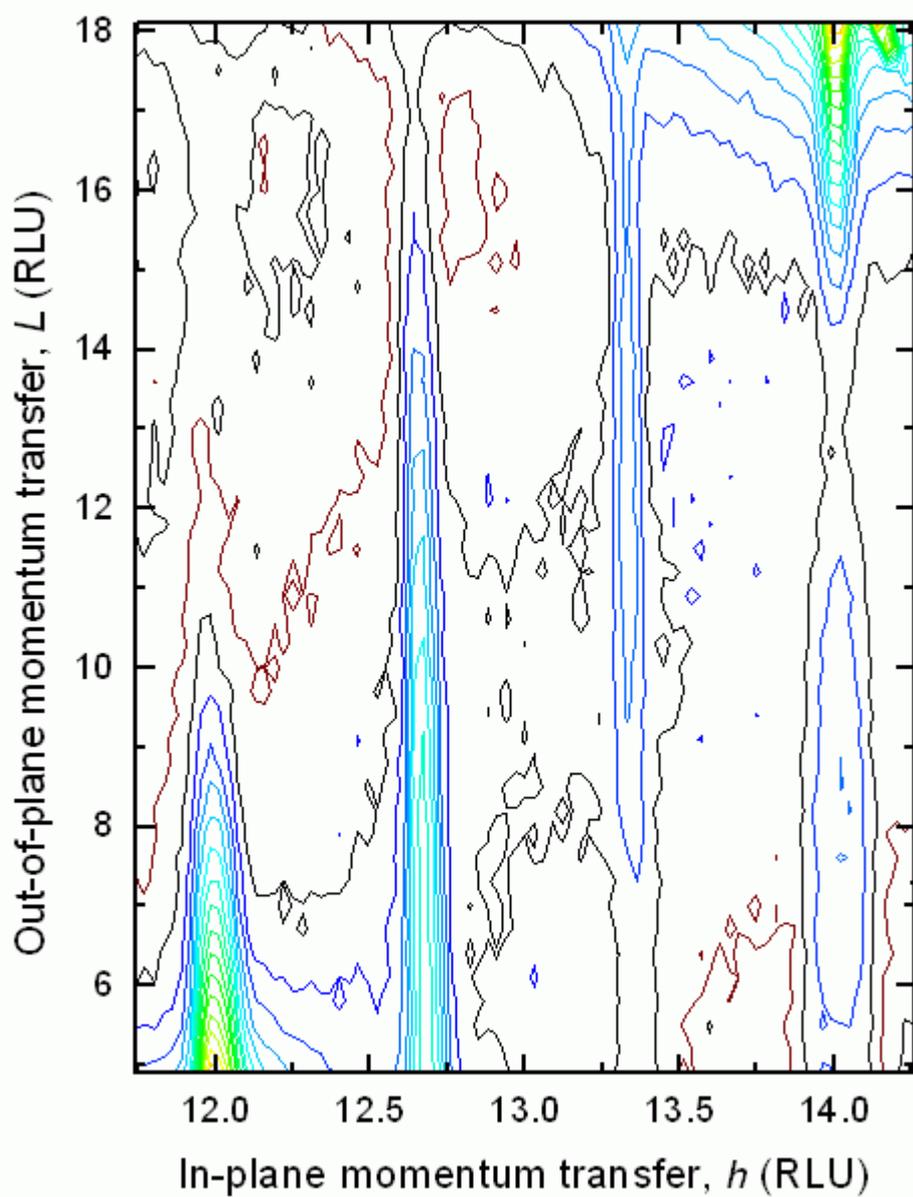


Figure 2. Contour plot showing some of the Crystal Truncation Rods of the clean Si(557) surface. Bragg peaks at positions (12,0,3) and (14,0,20) lie just off the top and bottom edges of the picture. Reconstruction rods due to the 1x3 surface lie in between.

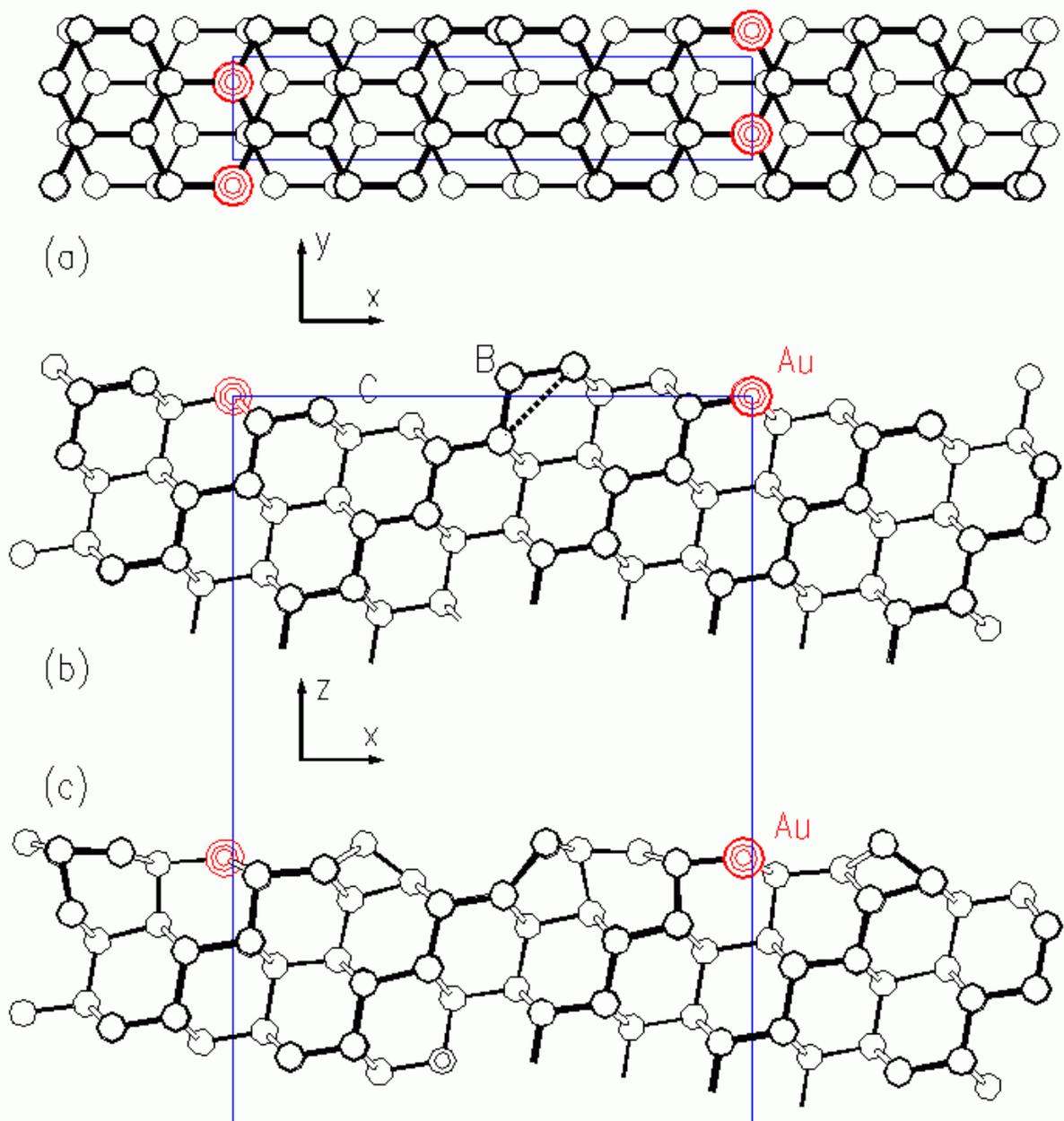


Figure 3. Top (x-y) and side (x-z) views of the structural model of the Au/Si(557) surface obtained by surface X-ray diffraction. The Au atoms are drawn as triple circles. Atoms and bonds closer to the observer are drawn with heavier lines for perspective.

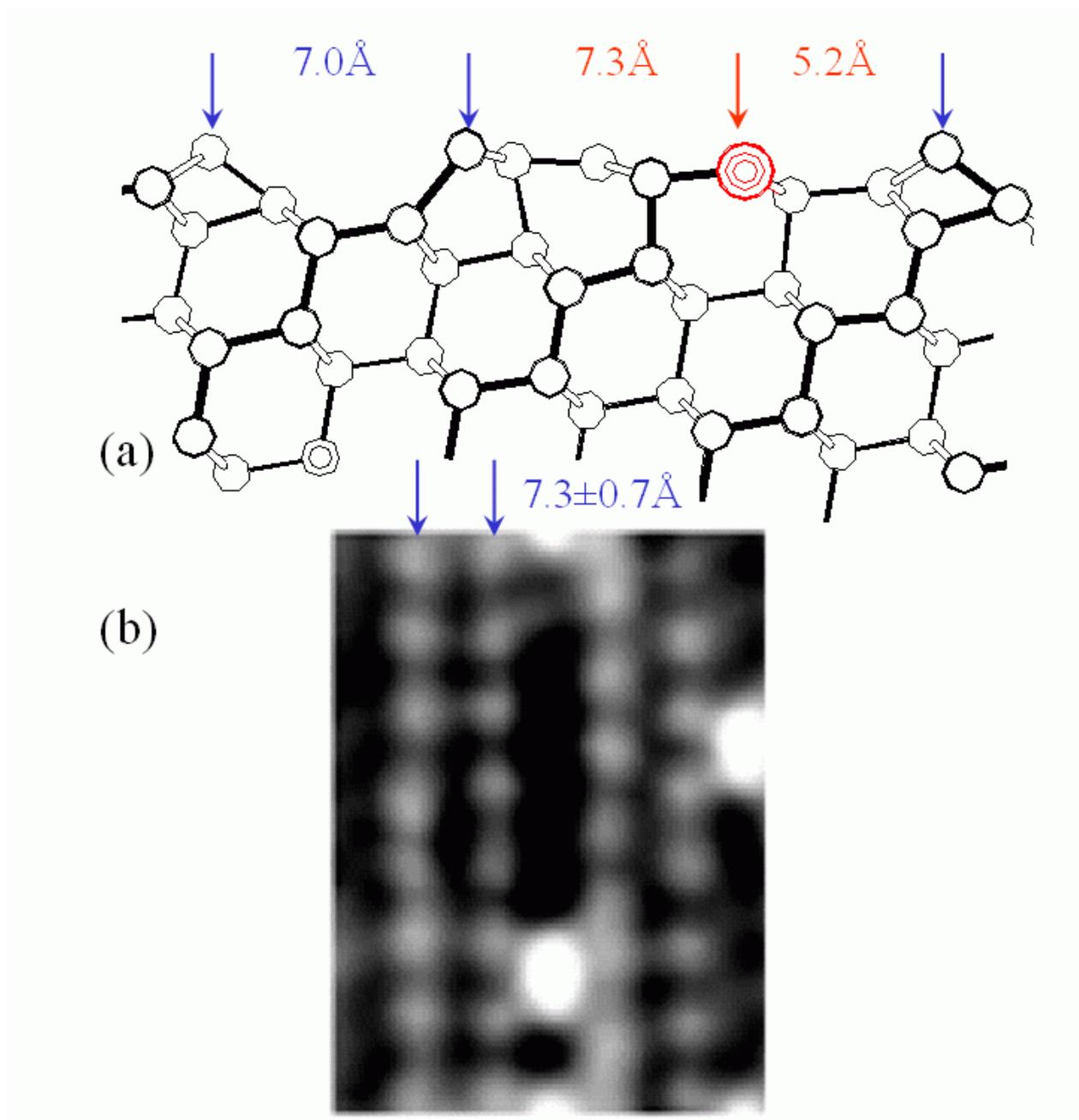


Figure 4. (a) Side (x-z) view of the refined structure of Au/Si(111) showing the spacings between the three most prominent features. An atom numbering scheme is introduced.

(b) STM image of Au/Si(111) showing the separation of the two rows of bright spots. The image represents a top view of the surface indicated by the x-y directions shown. The bright spots are identified here as Silicon atoms. The image was obtained using methods described in ref [5].

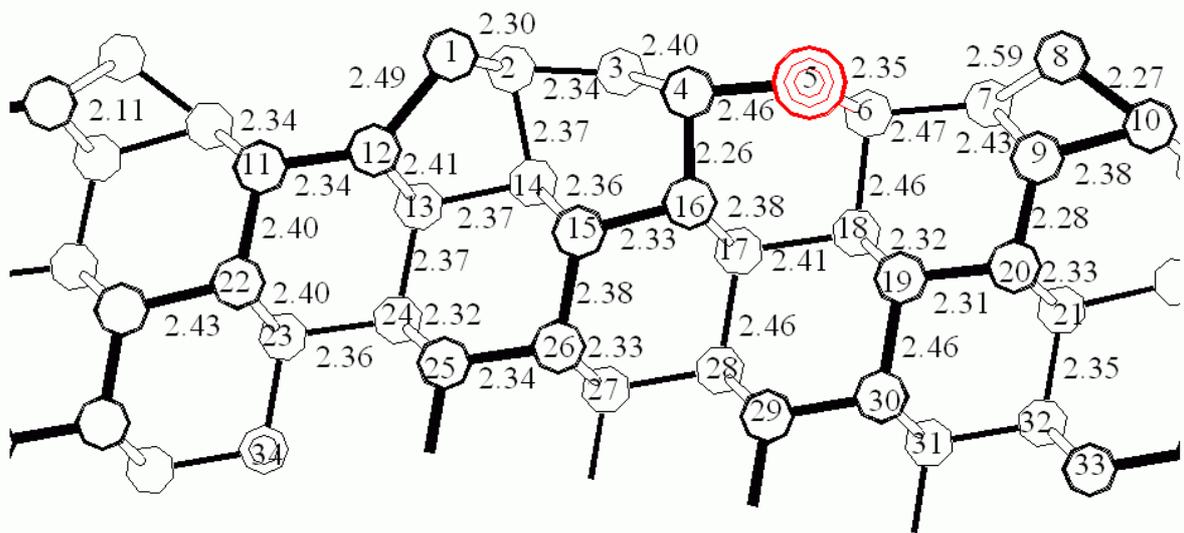


Figure 5. Side view of the refined structure of Au/Si(111) showing the numbering scheme and the bond lengths (in Å) between the atoms which were refined.

Table 1. Refined coordinates of the atomic positions using the numbering scheme of Fig 5. The coordinates are fractions of the orthorhombic unit cell constants, $a=38.208\text{\AA}$, $b=3.840\text{\AA}$ and $c=54.035\text{\AA}$. Two copies of each atom exist in the centered orthorhombic unit cell, related by the translation vector $(0.5,0.5,0)$. The column denoted B is the Debye-Waller factor in \AA^2 .

Atom	x	Y	z	B
1 Si	0.5134	0.5	0.1598	3.15
2 Si	0.5455	0.0	0.1544	3.15
3 Si	0.6040	0.0	0.1533	1.68
4 Si	0.6400	0.5	0.1456	0
5 Au	0.7042	0.5	0.1493	0
6 Si	0.7355	0.0	0.1375	0
7 Si	0.8000	0.0	0.1414	1.68
8 Si	0.8383	0.5	0.1587	0
9 Si	0.8255	0.5	0.1208	0
10 Si	0.8853	0.5	0.1330	1.68
11 Si	0.4123	0.5	0.1171	1.68
12 Si	0.4728	0.5	0.1237	1.68
13 Si	0.4964	0.0	0.1025	0
14 Si	0.5572	0.0	0.1114	0
15 Si	0.5816	0.5	0.0926	0
16 Si	0.6405	0.5	0.1038	0
17 Si	0.6667	0.0	0.0854	0
18 Si	0.7291	0.0	0.0922	0
19 Si	0.7529	0.5	0.0751	0
20 Si	0.8131	0.5	0.0796	0
21 Si	0.8384	0.0	0.0631	0
22 Si	0.4001	0.5	0.0735	0
23 Si	0.4242	0.0	0.0530	0
24 Si	0.4853	0.0	0.0594	0
25 Si	0.5101	0.5	0.0429	0
26 Si	0.5707	0.5	0.0493	0
27 Si	0.5960	0.0	0.0328	0
28 Si	0.6566	0.0	0.0404	0
29 Si	0.6818	0.5	0.0227	0
30 Si	0.7424	0.5	0.0303	0
31 Si	0.7677	0.0	0.0126	0
32 Si	0.8283	0.0	0.0202	0
33 Si	0.8535	0.5	0.0025	0
34 Si	0.4141	0.0	0.0101	0

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