

## ATOMIC STRUCTURE OF THE In ON Si(111)(4 × 1) SURFACE

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Received 13 November 1996

The atomic structure of the In on Si(111)(4 × 1) surface has been determined using direct methods applied to transmission electron diffraction data. It consists of a zigzag chain of In atoms and a region of silicon including a dimer chain. The structure is sufficiently similar to recent models of the Au on Si(111)(5 × 2) and metal on Si(111)(3 × 1) structures, that some preliminary generalizations on the linear  $n \times 1$  and  $n \times 2$  Si(111) reconstructions can be made.

### 1. Introduction

Metals on silicon surfaces are important both scientifically and technologically in terms of contacts and surfactant-mediated growth. One example of the latter is In on Si(111). While the bulk system is a simple eutectic with no stable phases,<sup>1</sup> at the surface a number of relatively stable structures are formed, such as  $\sqrt{3} \times \sqrt{3}$ ,<sup>2-13</sup>  $\sqrt{31} \times \sqrt{31}$ ,<sup>5,6,9-12</sup> and  $4 \times 1$ .<sup>6-19</sup> Studies indicate that the  $\sqrt{3} \times \sqrt{3}$  structure consists of 1/3 of a monolayer (ML) of In adatoms sitting in T<sub>4</sub> sites. Little is known about the  $\sqrt{31} \times \sqrt{31}$  structure other than that it has a higher In coverage than the  $\sqrt{3} \times \sqrt{3}$  reconstruction, and the  $4 \times 1$  structure remains unclear, with proposed models ranging from two to four In atoms within the unit cell (0.5-1 ML coverage). The strongest evidence for two In atoms comes from ion-scattering spectrometry (ISS) data.<sup>14,15</sup> Strongly conflicting with this are, among others, Auger<sup>16</sup> and photoemission<sup>18</sup> measurements reporting four In atoms. Scanning tunneling microscopy has provided some information, showing pairs of "lines" running along the "1" direction of the cell;<sup>11-14</sup> however, the images are not particularly good due to conduction problems. Very recently XPS and UPS<sup>18</sup> have indicated that rather metallic conduction exists along the "1" direction, while the "4" direction is semiconducting. At least to

date, the possibility of additional silicon rearrangements has not been considered. All of the currently proposed models consist of In adatoms sitting on top of an unreconstructed Si double layer. An STM study by Tanishiro *et al.*<sup>11</sup> has suggested that the number density of silicon atoms involved in the reconstruction is 2 ML.

For bulk structure determination, the standard technique is X-ray diffraction coupled with direct methods. Until very recently it was believed that this approach would not work for surfaces, but we have been able to use it for Au on Si(111)  $\sqrt{3} \times \sqrt{3}$  and  $5 \times 2$  surfaces<sup>20</sup> as well as the Si(111)(7 × 7) reconstruction.<sup>21</sup> In all of these the main fragments of the surface were already known, so in part these were reliability checks. In this paper we use this technique for a completely unknown structure, the In on Si(111)(4 × 1) surface. The structure determination turns out to be relatively simple, and the atomic coordination very similar to the Au on Si(111)(5 × 2)<sup>22</sup> and to several recently proposed models for adsorbates on Si(111)(3 × 1) surfaces,<sup>23-29</sup> suggesting that some generalizations can be made.

### 2. Experimental Method

TED patterns of Si(111)(4 × 1)-In were taken using the selected-area diffraction mode of a 100 kV UHV

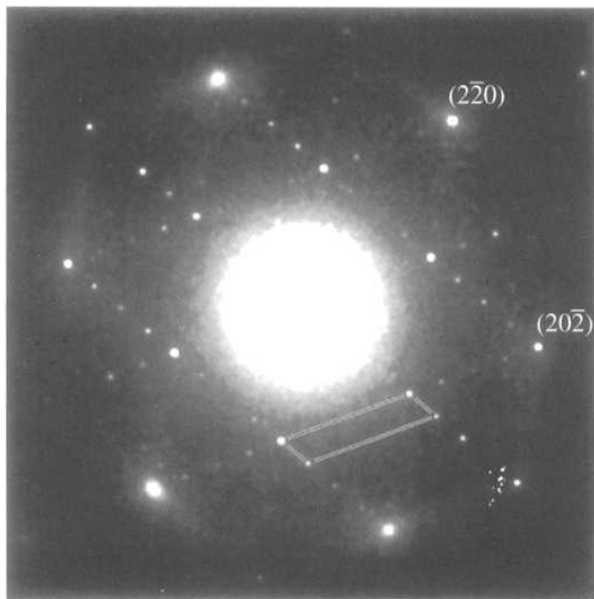


Fig. 1. Si(111)(4 × 1)-In diffraction pattern recorded on an image plate. Three separate domains of 4 × 1 are present. The 4 × 1 unit cell for one domain is outlined.

electron microscope.<sup>30</sup> Specimens were cut in a form of  $7 \times 1 \times 0.4 \text{ mm}^3$  from a Si(111) wafer. The technique to make thin areas in silicon substrate films for TEM-TED observations was described previously:<sup>31</sup> a hollow was made mechanically in the wafer, and the bottom of the hollow thinned by DC heating and oxygen gas etching in the microscope. A mean thickness of about 1 ML of indium (as measured by a quartz oscillator) was first deposited onto the specimen at about 300°C and the surface structure changed from  $7 \times 7$  to “1 × 1.” By annealing at 450°C, some indium desorbed and the surface structure changed to  $\sqrt{3} \times \sqrt{3}$ . The coverage of  $\sqrt{3} \times \sqrt{3}$  is considered to be 1/3 of an ML. By redeposition of 0.4–0.5 ML of indium on the surface at 300°C, the 4 × 1 structure was formed. TED patterns were recorded on Fuji FG films and imaging plates. Figure 1 is a diffraction pattern from one of the imaging plates.

### 3. Numerical Method

We worked with two data sets, the first recorded on film and reduced in Tokyo, the second recorded on an image plate in Tokyo and reduced using a cross-correlation technique<sup>32</sup> at Northwestern. The measured magnitudes of the structure factors of the

Table I. A comparison of the eight strongest beams in the Si(111)(4 × 1)-In data sets with the values calculated from the proposed model. The image plate data set was used in the fitting procedure to refine the model. The magnitudes of the structure factors are relative values. The two data sets were taken under different conditions of specimen thickness and crystal tilt.

$h$	$k$	$ F $ (image plate)	$ F $ (film)	Calculated
6	0	8.3	8.3	8.3
3	1	7.1	7.4	7.1
5	0	6.1	6.8	6.0
5	1	5.4	6.1	5.4
4	1	4.8	5.4	4.8
1	1	3.9	4.9	3.5
6	2	2.7	3.0	3.7
9	1	2.4	2.7	2.4

strongest beams are listed in Table I for each data set along with the values calculated from the proposed model. Since the diffraction pattern displayed p2mm symmetry, it was natural to perform the analysis within a rectangular unit cell with the  $a$  axis along  $[\bar{1}\bar{1}2]$  ( $A = 13.30 \text{ \AA}$ ) and the  $b$  axis along  $[1\bar{1}0]$  ( $B = 3.84 \text{ \AA}$ ). Strictly speaking, this rectangular unit cell is not a 4 × 1 unit cell with respect to the Si(111)(1 × 1) surface unit mesh. However, for convenience we will refer to the unit cell as 4 × 1 with the understanding that the cell is rectangular with the dimensions listed above. Within the Patterson point group p2mm a total of 27 different intensities were measured. These were then analyzed using a Sayre equation with unitary structure factors, and a normalized least squares figure of merit (FOM) used to gauge the validity of the phasing solutions (more details are given below). Although the symmetry of the structure is not completely known, ICISS<sup>15</sup> and RHEED<sup>16</sup> data have suggested glide or mirror planes parallel to  $[\bar{1}\bar{1}2]$  (the “4” direction). A glide plane along this direction seems unlikely, since its existence would require the extinction of all  $(h, 0)$  reflections, where  $h$  is odd (referenced to a 4 × 1 unit cell), and the TED data show significant intensities at these points. Accordingly, the diffraction pattern was analyzed with the three possibilities of p2mm, pm and p2mg with a 1 × 4 unit cell. We also noted that the (0, 1) reflection (referenced to a 4 × 1 cell) is too weak to be detected in the TED pattern. With a

mirror along the  $[\bar{1}\bar{1}2]$  direction, the absence or near-absence of the (0,1) spot suggests that the scattering potential on each of the two mirror planes within a unit cell is the same or nearly the same. Alternatively, without a mirror along the  $[\bar{1}\bar{1}2]$  direction, the extinction of the (0,1) spot could be caused by a glide plane parallel to  $[1\bar{1}0]$ . For completeness, pg symmetry with a  $4 \times 1$  unit cell was also investigated. As a final step, R factor and  $\chi^2$  minimizations were performed to give a more accurate location of the atoms within a kinematical model.

#### 4. Results

When using direct phasing methods, one attempts to find a solution to the phase problem by using probability relationships between the intensities and the phases of the diffracted beams. Through an iterative numerical process, a set of phases for the measured beams is assigned which best satisfies these probability relationships. The FOM's presented in this paper are measures of how well a given set of phases satisfies the probability relationships. We will discuss here, briefly, how the crystallographic analysis was performed, for simplicity using a  $4 \times 1$  cell. First, we fixed the (3,1) spot as the origin definer. From this, the strong sigma-1 relationship to the (6,0) and (6,2) spots fixed the phases of these. Next, analyzing the sigma-1 relationships it was apparent that the (0,2) spot [which is coincident with a bulk (220) diffraction spot] was strong. Although not measured, we will later use this information and the knowledge that its phase is  $\pi$  in p2mg ( $2\pi$  in pm) in presenting the potential maps. There are then four other strong spots in the diffraction pattern, namely (5,0), (5,1), (4,1) and (1,1).

For the centrosymmetric p2mm and p2mg cells, origin definition requires two beams and the phase of (5,0) can be fixed along with (3,1). This leaves eight possible permutations for the phases of (5,1), (4,1) and (1,1) ( $\pi$  or  $2\pi$  each). For the non-centrosymmetric pm and pg cells, the strong beams were scanned in steps of  $5^\circ$  using a genetic algorithm.<sup>33</sup> The p2mm cell failed to give any realistic solutions. A pg cell gave plausible results, but rather noisy, and so will not be discussed further. Both p2mg and pm gave good results. It should be noted that the symmetry of the underlying Si double layer within a  $1 \times 4$

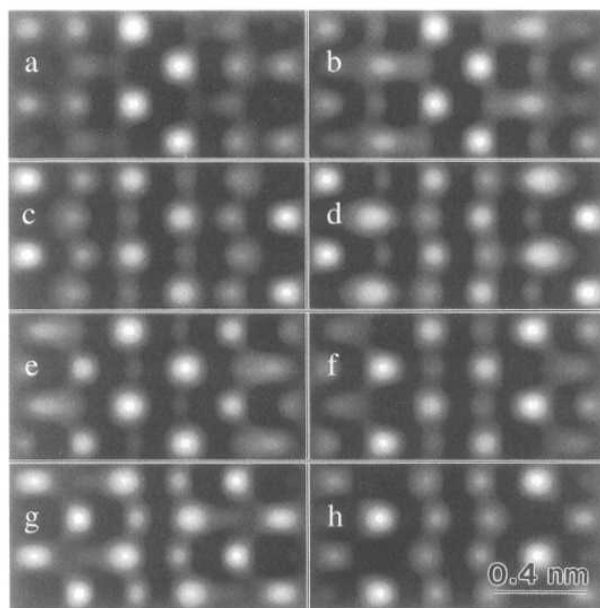


Fig. 2. Images of the scattering potential for the eight possible permutations of the phases of (5,1), (4,1) and (1,1) with p2mg symmetry. The (3,1) and (5,0) spots have been fixed to define an origin, (6,0) and (6,2) have been assigned phases based on the phase of (3,1) as explained in the text, and an estimate of the (0,2) spot magnitude has been included.

unit cell is pm, and that p2mg is a higher symmetry group within pm.

To give a qualitative overview of the possible structures, Fig. 2 shows the eight permutations in p2mg restricted to the origin-defining beams as well as the three strong beams mentioned above. To clarify the possible atomic sites, a (0,2) structure factor estimated at two-thirds of the (6,0) has been included. We should caution the reader not to over-interpret these maps, since one should rely more upon the good FOM results shown later. While there are some plausible models with four In atoms [e.g. Fig. 2(f)], only one of the models [Fig. 2(a)] has strong potential at possible In sites and appropriately weak possible Si sites. In most of the others the atomic configurations are also chemically unrealistic, for instance the “double  $\pi$  chain” in Fig. 2(h).

More rigorous are the full optimized FOM results shown in Fig. 3 for the space groups p2mg and pm. The results were quite conclusive; other phase combinations gave much worse FOM's. The solutions for the two symmetries are almost identical, except

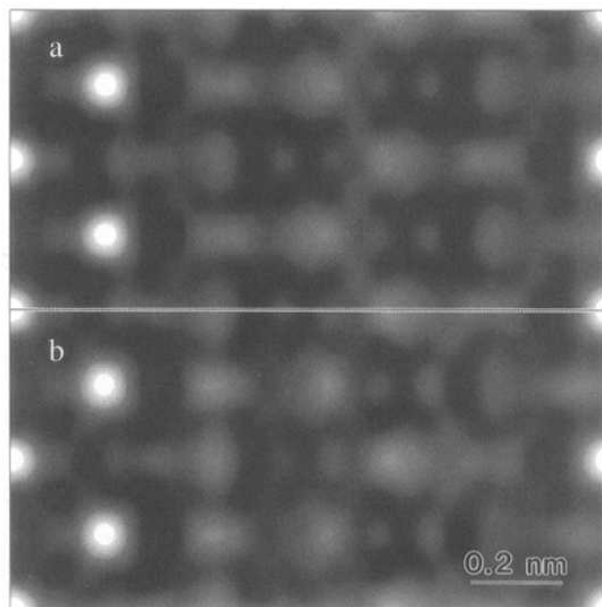


Fig. 3. Images of the scattering potential for fully optimized FOM results. (a) p2mg symmetry; (b) pm symmetry.

for a small double positioning in the p2mg results. (As pointed out by R. E. Marsh,<sup>34</sup> it is often better to use a higher symmetry group for the initial analysis.) These correspond to the structure shown in Fig. 4, where the actual atom positions are based upon kinematical refinements and are as shown in Table II. The refined structure has pm symmetry. For the final stage of the kinematical refinements, a multilayer strain field was used to model displacements into the substrate.<sup>35</sup> The strain field is constrained to decay exponentially into the bulk, and 2.5 Si double layers were included in the calculations. The analysis presented here provides no information about the position of atoms perpendicular to the Si(111) surface, and the height of the In atoms above the top Si plane shown in Fig. 4 (1.15 Å) is based on the value measured in the ISS study of Cornelison *et al.*<sup>15</sup> With a second Si double layer included in the initial stages of the fitting procedure (15 fitting parameters), the R factor was reasonable at  $R = 0.24$ , and the  $\chi^2$  value fair at about 3. In the final fit using the multilayer strain field, the R factor dropped to  $R = 0.14$ . Eighteen parameters were required to describe the multilayer strain field. It should be noted that with only 27 data points, the exact atomic positions within a

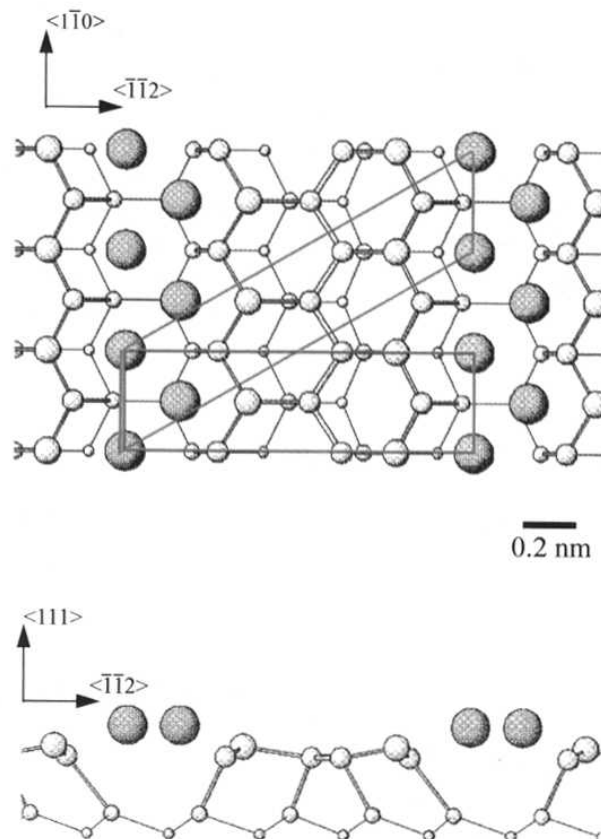


Fig. 4. Proposed model for the Si(111)(4 × 1)-In structure based on the direct phasing results. The final atom positions have been determined by fitting the diffraction pattern intensities with an R factor minimization in the kinematical approximation assuming pm symmetry. The large, dark spheres are the In atoms. The positions of the Si atoms along the [111] direction have been estimated from their bulk values, and the height of the In above the top layer of Si has been fixed at  $\sim 1$  Å in accordance with the ISS study of Cornelison *et al.*<sup>15</sup> A standard 4 × 1 unit cell is outlined in blue, while the rectangular unit cell used in our analysis is shown in red.

model fit with 18 parameters should be viewed with some caution. However, full information for a complete dynamical refinement of the structure was not available. The lack of a dynamical refinement makes a precise error analysis impractical, since the errors associated with making the kinematical approximation are unknown. As a rough gauge of the uncertainty we performed the minimization using both an R factor and a  $\chi^2$  factor, and the differences in the atom positions found in the two cases were around 0.1 Å. The displacements away from bulk

Table II. Atom positions found in R factor refinement as discussed in the text. The  $x$  axis is taken along the  $[\bar{1}\bar{1}2]$  direction shown in Fig. 4, and the  $y$  axis is along the  $[1\bar{1}0]$  direction. The positions of the Si atoms along the  $[111]$  direction have been estimated from their bulk values, and the height of the In above the top layer of Si has been fixed at  $\sim 1$  Å in accordance with the ISS study of Cornelison *et al.*<sup>15</sup> The positions are listed in terms of the unit cell with dimensions of  $A = 13.30$  Å,  $B = 3.84$  Å, and  $C = 9.40$  Å.

Atom type	$x$	$y$	$z$
In	0.00	0.0	0.000
In	0.85	0.5	0.000
Si	0.22	0.0	-0.087
Si	0.66	0.5	-0.087
Si	0.38	0.0	-0.130
Si	0.46	0.5	-0.130
Si	0.18	0.5	-0.130
Si	0.71	0.0	-0.130
Si	0.28	0.0	-0.367
Si	0.05	0.5	-0.367
Si	0.79	0.0	-0.367
Si	0.52	0.5	-0.367
Si	0.12	0.0	-0.450
Si	0.37	0.5	-0.450
Si	0.61	0.0	-0.450
Si	0.87	0.5	-0.450

sites appear to be chemically reasonable — the silicon atoms on either side are pulled in towards the dimer chain.

## 5. Discussion

The main difference between the currently proposed model and previously proposed models is the inclusion of silicon atoms in the reconstructed overlayer. The  $1/2$  ML coverage for the currently proposed model agrees with the coverage for the model proposed by Cornelison *et al.*<sup>15</sup> and J. L. Stevens *et al.*<sup>14</sup> However, in the Cornelison model the In adsorbs on  $T_4$  and  $H_3$  sites without any Si atoms participating in the reconstruction. Another  $4 \times 1$  model, proposed by N. Nakamura *et al.*<sup>16</sup> and refined by M. S. Finney *et al.*,<sup>17</sup> consists of 1 ML of In adsorbed on  $T_4$  and  $H_3$  sites of an unreconstructed Si double layer. M. S. Finney *et al.* justify a coverage of 1 ML by showing a Patterson function and pointing

out that it contains too many peaks to be explainable with a  $1/2$  ML coverage. While this is true if one assumes that no Si participates in the reconstruction, the inclusion of Si atoms allows a consistent explanation of the Patterson function. We visually compared the Patterson map calculated from our electron diffraction data with the map shown in the X-ray diffraction paper by Finney *et al.* and found an excellent agreement.

One interesting general feature of our results is the marked similarity of the structure to both Si(111)(5 × 2)-Au and recently proposed models for the Si(111)(3 × 1) family of structures; in the former one has a double Au chain with a slightly longer Si unit, in the latter a single adsorbate chain and a shorter Si unit. The Si(111)(3 × 1) reconstruction can be induced by the alkali metals, Ag and CaF<sub>2</sub>. The similarity of LEED I-V scans<sup>36</sup> and STM images<sup>37</sup> for these different adsorbates implies that the same basic structure is present in all of the  $3 \times 1$  systems mentioned here. Weiering *et al.*<sup>23</sup> proposed a general model for the  $3 \times 1$  reconstruction consisting of a  $\pi$ -bonded Seiwatz<sup>38</sup> chain of Si and a single row of metal atoms sitting in  $T_1$  sites. The same structure was proposed to explain photoemission data on Si(111)(3 × 1)-K,<sup>24</sup> X-ray scattering data on Si(111)(3 × 1)-CaF<sub>2</sub>,<sup>25</sup> and STM images of Si(111)(3 × 1)-Ag.<sup>27</sup> Alternative models also involving  $\pi$ -bonded Si chains have been proposed by Okuda *et al.*<sup>28</sup> based on photoelectron spectroscopy measurements of Si(111)(3 × 1)-Na, by Ohnishi *et al.*<sup>29</sup> based on STM observations, and by Erwin<sup>26</sup> based on total energy calculations for the alkali metals on Si(111). The model proposed by Erwin (also one of the Okuda models) consists of a modified Pandey chain<sup>39</sup> with the adsorbate atoms sitting on top of a reconstructed Si double layer. Erwin used numerically simulated STM images of the structure to show that the adsorbate atoms do not show up as intensity maxima in either the filled state or empty state pictures. The intensity maxima in the filled state image corresponded to the two highest Si in the reconstructed Si double layer, and both the filled and empty state images were consistent with experimental STM results. Regardless of which model for the  $3 \times 1$  surface is correct, the recently proposed structures all involve a Si chain, and it is generally accepted that a single structure will be able to explain the majority of the Si(111)(3 × 1) systems.

The current study suggests that the general nature of the linear  $n \times 1$  and  $n \times 2$  reconstructions on Si(111) is not limited to the  $3 \times 1$  family. Our proposed  $4 \times 1$  structure contains a Si chain lying in-between rows of metal atoms. The bonding of the In atoms differs from the monovalent species forming the  $3 \times 1$  structure, and a zigzag chain of In atoms is created rather than a single line of Ag, alkali metal or  $\text{CaF}_2$ . In the Si(111)( $5 \times 2$ )-Au system, double rows of Au form and the partial Si layer between the Au rows simply extends a bit further than in the  $4 \times 1$  structure.

## 6. Acknowledgments

We would like to acknowledge the support of the National Science Foundation through grant #DMR-92145505 and the support of the Ministry of Education, Science and Culture through Grant-in-Aid for Scientific Research (#06650038 and #07504004) in funding this work.

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