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Si(111)-(4x1) reconstruction by surface x-ray
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Structure determination of the indium-induced Si(111)-(4×1) reconstruction by surface x-ray diffraction

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A detailed structural model for the indium-induced Si(111)-(4×1) surface reconstruction has been determined by analyzing an extensive set of x-ray-diffraction data recorded with monochromatic ($\hbar\omega = 9.1$ keV) synchrotron radiation. The reconstruction is quasi-one-dimensional. The main features in the structure are chains of silicon atoms alternating with zigzag chains of indium atoms on top of an essentially unperturbed silicon lattice. The indium coverage corresponds to one monolayer. The structural model consistently explains all previously published experimental data.

Considerable interest has focused recently on adsorbate-induced modification of semiconductor surfaces as a technique to create nanoscale quantum structures of high perfection. In this paper we report the formation of quasi-one-dimensional (1d) chains on the (4×1)-reconstructed Si(111) surface induced by the adsorption of indium and present the atomic structure as determined by surface x-ray diffraction (SXRD).

Several surface reconstructions are induced by indium on Si(111) (see, e.g., Kraft *et al.*, Ref. 1) depending on the coverage; the Si(111)-(4×1)-In reconstruction marks the borderline between the semiconducting, low indium coverage, and metallic, high-coverage, phases.¹ Despite the fact that the indium-induced Si(111)-(4×1) reconstruction was reported for the first time by Lander and Morrison in 1965² and has been investigated with a variety of techniques subsequently, no definitive structural model could be established to date and some of the experimental results are apparently inconsistent.

In direct³ and inverse⁴ photoemission investigations on single-domain samples and recently in inverse photoemission investigations on a three-domain sample⁵ the Si(111)-(4×1)-In reconstruction showed a quasi-1d metallic behavior. Additionally to this interesting electronic property the surface exhibits an image state that also showed quasi-1d behavior in its strongly anisotropic dispersion: Along a certain direction the dispersion is very well described by a free electron parabola whereas in the perpendicular direction the dispersion falls below the free electron parabola.⁶ Scanning tunneling microscopy (STM) investigations of the Si(111)-(4×1)-In reconstruction^{1,7-11} resolved zig-zag chains running in the $\bar{1}10$ directions in the filled-state images and linear chains in the empty-state images. Tunneling data was acquired at bias voltages down to 0.04 V consistent with metallic behavior in agreement with scanning tunneling

spectroscopy results.¹ Adsorbed hydrogen was found to displace the indium atoms.⁹⁻¹¹ Filled-state STM images of the hydrogenated substrate show a (4×1) reconstruction with straight chains instead of the broad zigzag chains on the indium-terminated surface.⁹⁻¹¹ From these observations and results found in the literature Saranin *et al.*⁹ proposed a structural model. This model as well as the model derived by Collazo-Davila *et al.*¹² by applying direct methods to transmission electron diffraction (TED) data are at variance with the x-ray photoelectron spectroscopy (XPS) results of Abukawa *et al.*¹³ Since the core-level spectra did not show peaks corresponding to surface silicon atoms a complex substrate reconstruction can be ruled out.

All the inconsistencies between the earlier experimental results are eliminated with our structural model. The determination of the geometric structure lays the foundation for a theoretical investigation of the interesting electronic structure of this system.

We used the well established experimental technique SXRD to determine the structure of the Si(111)-(4×1)-In reconstruction. To minimize the uncertainties induced by not well controlled sample preparation conditions we employed the unique combination of an ultra high vacuum (UHV) system equipped with standard techniques like reflection high energy electron diffraction and low energy electron diffraction (LEED) facilities close to the wiggler beamline BW2 at HASYLAB (Hamburger Synchrotronstrahlungslabor) and a portable UHV chamber for the SXRD measurements.

We used p-type (B doped) Si(111) wafers (Wacker Chemie) with a resistivity of 7 Ω cm and nominally no miscut. STM measurements on the clean Si(111)-(7×7) surface showed domain sizes of more than 10000 Å so the miscut was less than 0.02°. The carefully outgassed sample was cleaned repeatedly by 'flashing' to $\sim 1150^\circ\text{C}$

for 15-20 s and slow cooling from 900°C to room temperature. Indium was deposited from a Knudsen cell at a rate of ~ 0.4 ML/min on the sample at $\sim 500^\circ\text{C}$ until the $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction was observed; at this stage the stacking fault of the Si(111)-(7 \times 7) reconstruction was removed. Further deposition at a lower temperature of $\sim 430^\circ\text{C}$ (with a lower probability for indium desorption) yielded first the $(\sqrt{31} \times \sqrt{31})$ and finally the (4 \times 1) reconstruction. The sample was transferred in a portable UHV chamber to the wiggler beamline BW2 at HASYLAB for the x-ray diffraction measurements. The incident monochromized x-rays with an energy of 9.1 keV impinged on the sample at a grazing angle of 0.5° . An in-plane data-set of 296 reflections with $l = 0.07$ was recorded by rotating the crystal about the surface normal. The background subtracted integrated intensities were corrected for the Lorentz factor, polarization factor, active sample area and the rod interception appropriate for the z-axis geometry.¹⁴ In SXRD measurements the fractional-order reflections which belong to one domain do not overlap with the reflections which belong to the other two rotational domains. By comparing equivalent fractional-order reflections the areas of the three rotational domains were found to correspond to 25%, 37% and 38% of the total surface area. The equivalent rescaled fractional-order reflections were averaged under the assumption of mirror-lines running along $\langle 11\bar{2} \rangle$ and a systematic error of $\epsilon = 13.7\%$ was determined. The rods were scaled according to the corresponding in-plane intensity and therefore only one overall scale factor was necessary for the data analysis. In total the data-set consists of 550 symmetry inequivalent reflections, 61 along two crystal truncation rods (ctrs), 337 along 11 fractional-order rods and 152 in-plane reflections.

In the following we use LEED coordinates with $\mathbf{a} = 1/2[10\bar{1}]_{\text{cubic}}$, $\mathbf{b} = 1/2[\bar{1}10]_{\text{cubic}}$ and $\mathbf{c} = 1/3[111]_{\text{cubic}}$. The cubic coordinates are in units of the silicon lattice constant (5.43 Å) and therefore $|a| = |b| = 3.84$ Å and $|c| = 3.14$ Å. The absolute values of the reciprocal coordinates including a factor of 2π are $|a^*| = |b^*| = 1.89$ Å⁻¹ and $|c^*| = 2.00$ Å⁻¹.

Usually the first step in the analysis of surface diffraction data is to plot the Patterson function, i.e. the pair correlation function of the electron density. The Patterson function projected in the surface plane can be calculated from the in-plane reflections which have a small momentum transfer perpendicular to the surface. A contour plot of this function is shown in Fig. 1 and is qualitatively in good agreement with that previously reported by Finney *et al.*¹⁵ Each peak in the Patterson function corresponds to an important interatomic vector in the surface reconstruction. Since indium ($Z^2 = 49^2$) is a much stronger scatterer than silicon ($Z^2 = 14^2$) the peaks correspond to interatomic vectors between indium atoms. The three interatomic distance vectors which can be seen in the Patterson function in Fig. 1 indicate that at least three different indium sites must be involved in the recon-

struction. It is highly unlikely that the indium coverage can be 0.5 ML (monolayer) since that would only correspond to two indium atoms per unit cell. It has been argued that a reconstruction of the substrate might lead to further peaks in the Patterson function¹² but the XPS data¹³ make this unlikely.

During the course of the data analysis we tested several possible initial indium atom configurations and determined the substrate structure in the subsequent refinement. The model found is shown in Fig. 2. The correctness of the model is proven both by the good agreement of the measured data with the intensities calculated from the model structure shown in Fig. 3 and by the overall reduced χ^2 value of 1.5. We will now describe the building blocks of the model and resolve some of the apparent inconsistencies between the previously reported experimental results.

The model shown in Fig. 2 consists of a zigzag chain of silicon atoms as found in the π -bonded chain model for the (2 \times 1) reconstruction of the Si(111) surface¹⁶ on top of an essentially unreconstructed substrate. This model is consistent with the XPS investigations which showed that no strong silicon surface component was present in the Si 2*p* spectra.¹³ Even in the absence of indium atoms the silicon chains on the substrate possess a (4 \times 1) periodicity and it is highly likely that the chains observed after hydrogen adsorption^{9,11} are made up of silicon atoms. The Si(111)-(4 \times 1)-In reconstruction is completed by adding two zigzag rows of indium atoms in the space between the silicon chains. The arrangement of the indium atoms is similar to the arrangement proposed on the basis of μ -probe Auger electron diffraction investigations,¹⁷ and also used in a previous SXRD study.¹⁵ There are two inequivalent types of indium atoms in agreement with the XPS results.¹³ The indium atoms next to the silicon chains are probably covalently bonded to the silicon chain atoms. For the inner indium atoms the bonding configuration is not so obvious. In Fig. 2 a bonding configuration of covalent $p_{x,y,z}$ bonds to the neighboring indium atoms and down to the silicon substrate under an angle of approximately 90° are shown. The nearest neighbor distance of the indium atoms is within the range of 2.98 Å to 3.14 Å. Electron counting can not be strictly applied to determine the bonding configuration because the surface has 1d metallic character. If we assume that the bonding configuration shown in Fig. 2 is a first approximation to the more complex real configuration then it is evident that the surface free energy of this reconstruction is lower than for other models since there are no silicon dangling bonds and all the group III indium atoms are trivalently bonded. The present SXRD data do not permit an accurate determination of the bond charge densities; the detailed bonding configuration will have to be the subject of a future theoretical investigation.

An important question is how the model shown in Fig. 2 with four indium atoms per unit cell (1 ML) can be used to explain the results of the TED¹² and impact colli-

sion ion scattering spectrometry (ICISS) investigations⁸ which resulted in models with only two indium atoms per unit cell. In the TED study direct methods were used to analyze the data and electron density maps with indium atom configurations compatible with the TED data were presented including plausible configurations with four indium atoms (e.g. Fig. 2 (f) in Ref. 12). The 1/2 ML model which was compatible with the TED data is at variance with the SXRD data as shown in Fig. 3 (c) where the dashed lines calculated using the 1/2 ML model do not reproduce the measured data adequately. A preliminary data analysis of the SXRD data using direct methods resulted in the indium atom configuration shown in Fig. 2 thereby indicating the correctness of our model.¹⁸ The TED data were not sufficient to include dynamical diffraction effects and the resolution was probably not good enough to rule out the wrong indium atom configuration.¹⁸ The reduced χ^2 value for the model proposed by Saranin *et al.*⁹ is 7.3 and therefore this model can also be definitely eliminated. The side view of the Si(111)-(4×1)-In reconstruction shown in Fig. 2(b) and the atomic coordinates given in Table I show that the atoms in the topmost layer have three different heights. The highest atoms are the indium atoms bonded to the silicon chain, the inner indium atoms of the indium “stripe” are lower and the silicon chain atoms are lowest. The existence of different heights is in agreement with the results of a previously performed STM investigation.¹¹ Low energy ion scattering is very sensitive to the topmost surface layer. The configuration of the topmost indium atoms bonded to the silicon chains strongly resembles the 1/2 ML model with indium atoms on H_3 and T_4 sites that has been found to reproduce the ICISS data collected using 2 keV Li^+ ions.⁸ Another 1/2 ML model with a zigzag chain of indium atoms on T_4 sites also gave reasonable agreement with the ICISS data⁸ since such chains are present in our model as shown in Fig. 2.

In summary, the structure of the Si(111)-(4×1)-In reconstruction has been determined using surface x-ray diffraction. The quasi-one-dimensional character of this surface reconstruction is given by zigzag chains of silicon atoms on top of an unreconstructed silicon substrate and four indium atoms per unit cell (1 ML) arranged in two zigzag chains in the gap between the silicon chains. The indium atom arrangement may also be regarded as being quasi hexagonal. We have shown that most of the previously published experimental data are consistent with the new structural model. We hope that the atomic coordinates given in Table I will pave the way for detailed theoretical investigations of the interesting electronic structure of this system.

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	position [LEED-coord.]	deviation \mathbf{d} [Å]	$ \mathbf{d} $ [Å]
In	(0.11,0.06, 0.86)		
In	(0.86,0.93, 0.85)		
In	(1.53,0.77, 0.99)		
In	(3.43,0.22, 0.99)		
Si	(2.28,0.14, 0.73)		
Si	(2.71,0.86, 0.76)		
Si	(0.31,0.65,-0.26)	(-0.11,-0.05,-0.03)	0.10
Si	(3.96,0.98,-0.00)	(-0.15,-0.08,-0.01)	0.13
Si	(1.30,0.65,-0.25)	(-0.12,-0.06, 0.01)	0.10
Si	(0.96,0.98, 0.04)	(-0.16,-0.08, 0.13)	0.19
Si	(2.29,0.64,-0.33)	(-0.17,-0.09,-0.24)	0.28
Si	(2.01,0.00,-0.03)	(0.03, 0.02,-0.10)	0.10
Si	(3.29,0.65,-0.23)	(-0.16,-0.08, 0.05)	0.15
Si	(2.95,0.97,-0.01)	(-0.20,-0.10,-0.03)	0.18
Si	(0.66,0.33,-1.24)	(-0.04,-0.02, 0.04)	0.07
Si	(0.33,0.67,-1.01)	(-0.01,-0.01,-0.02)	0.02
Si	(1.65,0.32,-1.26)	(-0.08,-0.04,-0.03)	0.07
Si	(1.32,0.66,-0.99)	(-0.06,-0.03, 0.03)	0.06
Si	(2.67,0.33,-1.27)	(0.00, 0.00,-0.05)	0.05
Si	(2.32,0.66,-1.04)	(-0.05,-0.03,-0.13)	0.14
Si	(3.66,0.33,-1.25)	(-0.04,-0.02, 0.00)	0.03
Si	(3.31,0.65,-0.98)	(-0.09,-0.05, 0.04)	0.09

TABLE I. The atom positions in the Si(111)-(4×1)-In reconstruction derived from the analysis of the SXRD data. The positions of the atoms are given in LEED coordinates, the deviations from the bulk-like positions and the absolute values of these deviations are given in Å. For the silicon atoms an isotropic Debye-Waller factor of 0.5 Å^2 and for the indium atoms of 4.5 Å^2 was used in the data analysis.

FIG. 1. Patterson function of the electron density projected in the surface plane calculated from the fractional-order in-plane reflections. The axes are scaled in LEED coordinates (1.0 corresponds to 3.84 Å). The distance vectors shown are 1. (0.69,0.85), 2. (1.42,0.71) and 3. (2.00,0.50). The dashed line from (0,0) to (2,1) indicates the mirror line (along $\langle 11\bar{2} \rangle$ in bulk coordinates).

FIG. 2. Ball and stick model of the Si(111)-(4×1)-In reconstruction in top (a) and side (b) views. Indium atoms are drawn dark grey, silicon atoms are drawn light grey. The contributions to the peaks of the Patterson function are shown by arrows. The standard LEED (4×1) unit cell is indicated by a dashed line. The dashed-dotted line along $[11\bar{2}]$ indicates a mirror line.

FIG. 3. Measured and calculated SXRD intensities: (a) in-plane with $l = 0.07$. The radii of the filled (empty) semi-circles are proportional to the measured (calculated) intensities. Hatched circles are scaled with a factor of 0.5. (b) Fractional-order rod-scans. The solid line is calculated using the model shown in Fig. 2 with the coordinates given in Table I. (c) Integer order rods. The dashed lines correspond to the intensities calculated using the best fit to the model proposed in Ref. 12.

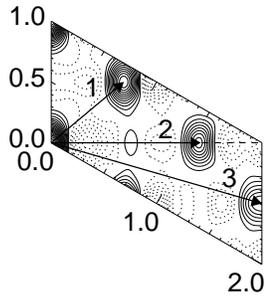


Fig. 1

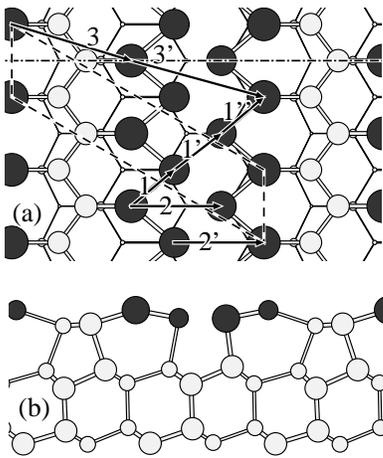


Fig. 2

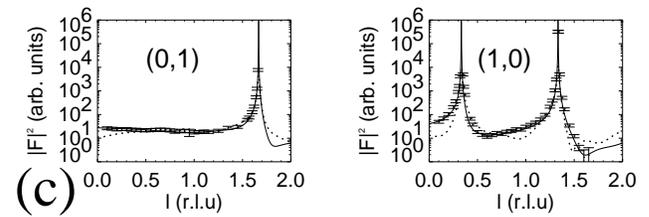
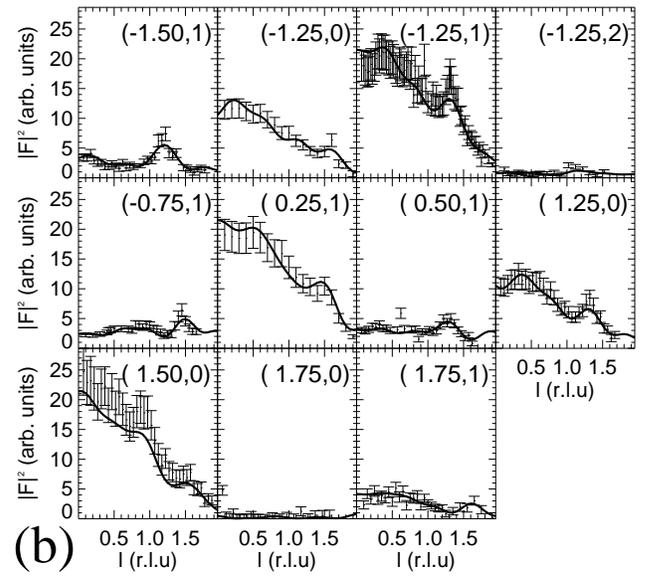
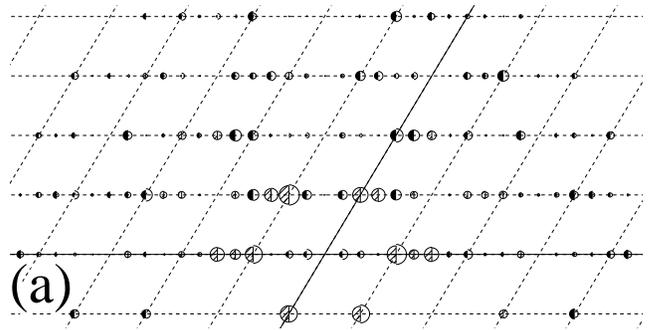


Fig. 3