

New Bonding Configuration on Si(111) and Ge(111) Surfaces Induced by the Adsorption of Alkali Metals

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The structure of the (3×1) reconstructions of the Si(111) and Ge(111) surfaces induced by adsorption of alkali metals has been determined on the basis of surface x-ray diffraction and low-energy electron diffraction measurements and density functional theory. The (3×1) surface results primarily from the substrate reconstruction and shows a new bonding configuration consisting of consecutive fivefold and sixfold Si (Ge) rings in $\langle 1\bar{1}0 \rangle$ projection separated by channels containing the alkali metal atoms. [S0031-9007(98)05973-0]

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Over the last decade there has been a large effort to understand the structure and properties of reconstructions on elemental semiconductor surfaces. The main driving force behind these reconstructions is the reduction of the number of dangling bonds without introducing too much strain in the surface region. Three structural elements meeting this principle have emerged so far. Particularly important are *adatoms* which saturate three dangling bonds on (111) surfaces while creating only one unsaturated bond. Adatoms stabilize the clean Ge(111)- $c(2 \times 8)$ surface [1] and are also a major stabilizing factor in the dimer-adatom-stacking-fault model of the clean Si(111)- (7×7) surface [2]. The second structural element that effectively reduces the number of dangling bonds is the *dimer* frequently found on the (001) surfaces [3]. The third structural element is the π -bonded chain which was first proposed for the clean Si(111)- (2×1) reconstruction [4]. Yet this simple principle has been of no utility in predicting surface structures as demonstrated by the metal induced (3×1) reconstructions on the (111) surfaces of Si and Ge. Despite the small unit cell, the atomic geometry is still unknown and has been heavily debated over the last ten years [5–13]. The mere observation of the symmetry-breaking (3×1) unit cell calls for a unidirectional structural motif and it was, therefore, appealing to introduce π -bonded chains to explain the 3×1 periodicity. At present, there are two promising models for the (3×1) reconstruction that have been proposed on the basis of scanning tunneling microscopy (STM) [8], electronic properties [9], and total-energy calculations [10]. The Seiwatz model [see Fig. 1(a)] [7,11,12] consists of parallel π -bonded chains formed by fivefold rings of Si (Ge) atoms in $\langle 1\bar{1}0 \rangle$ projection, separated by empty channels, with a top-site adsorbate saturating the surface dangling bonds. The

second model is the extended Pandey model [10,13] [see Fig. 1(b)] which consists of a sevenfold ring carrying the π -bonded chain alternating with a five and six-member ring of Si. It is intuitive to describe the ring sequences from these models with the notation 567567 (extended Pandey) and 500500 (Seiwatz model). Unfortunately, neither of these structures is able to explain our surface x-ray diffraction data (SXRD) or low-energy electron diffraction (LEED) data.

We determined the structure by using a multiple-technique approach involving SXRD, LEED, and density functional theory. This approach was mandatory in the

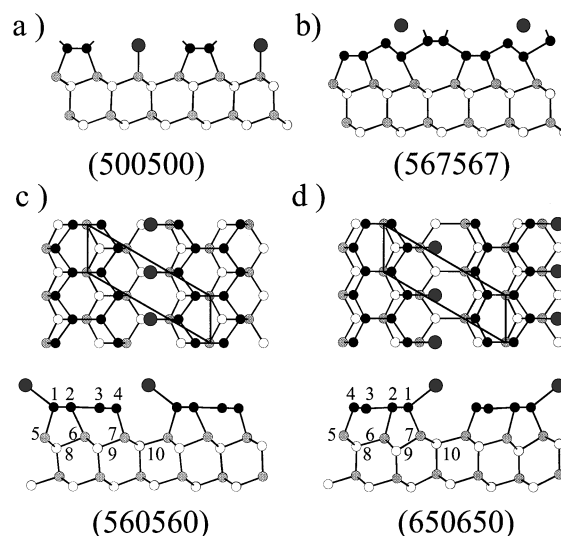


FIG. 1. Idealized schematic representations of the (a) Seiwatz model (500500) and the (b) extended Pandey model (567567) for the metal induced Si(111)- (3×1) reconstruction. Schematic representation of top and side views of the final structural 560560 and 650650 model are shown in (c) and (d).

present case in order to derive a correct and unique model. The model for the (3×1) structure consists of consecutive fivefold and sixfold Si (Ge) rings containing sp^2 bonded Si (Ge) atoms rather than forming π -bonded chains. The topmost Si (Ge) layer is nearly flat and exhibits only one dangling bond which is saturated by the alkali atom.

The density functional theory (DFT) calculations were performed using the local density approximation of Perdew and Wang [14] for the exchange-correlation functional. The action of the core electrons on the valence electrons was replaced by norm-preserving, scalar-relativistic pseudopotentials generated with Hamann's scheme [15]. The surface was modeled within the supercell approach, using 16 layers of Si and placing Li atoms on both sides of the slab.

LEED intensity measurements were performed at normal incidence at a sample temperature of 100 K for Si(111)- (3×1) -Li and at room temperature for Ge(111)- (3×1) -Li. A computer-controlled video camera was used to record integrated spot intensities of five integral-order beams and ten fractional-order beams (energy range 30 to 250 eV) from the fluorescence screen. The cumulative energy range was 1600 and 1500 eV for Si(111)- (3×1) -Li and Ge(111)- (3×1) -Li, respectively. LEED IV curves were calculated using the program code of Moritz [16] and were compared with the experimental LEED IV curves by applying an automated least-squares optimization scheme [17], based on Pendry's R factor R_P [18].

The SXRD measurements of the (3×1) structure of Na and Li on the Si(111) surface and of Rb on the Ge(111) surface were performed at the wiggler beam line BW2 at the Hamburg synchrotron radiation laboratory (HASYLAB) using a x-ray wavelength of 1.3 Å. The resulting in-plane data sets of Li/Si(111), Na/Si(111), and Rb/Ge(111) were averaged over symmetry related reflections, leading to final data sets of 17, 24, and 43 irreducible structure factor intensities, respectively. All reflections are indexed with respect to a reciprocal surface unit cell given by $\mathbf{b}_1 = \frac{1}{2}[1, 0, \bar{1}]_{\text{bulk}}$, $\mathbf{b}_2 = \frac{1}{2}[\bar{1}, 1, 0]_{\text{bulk}}$ in the surface plane, and $\mathbf{b}_3 = \frac{1}{3}[1, 1, 1]_{\text{bulk}}$ normal to the surface. For the out-of-plane analysis six, twelve, and sixteen fractional-order rods were measured for the Li/Si(111), Na/Si(111), and Rb/Ge(111) samples, respectively. In spite of the dramatic differences in atomic size and scattering factors for Li, Na, and Rb, the measured structure factor intensities along the fractional-order rods for the (3×1) reconstruction of Li/Si(111), Na/Si(111), and Rb/Ge(111) are essentially identical as shown in Fig. 2. The in-plane data are also nearly identical to those obtained by SXRD on a Si(111)- (3×1) surface induced by chemisorption of CaF₂ [12]. Therefore, the main part of the reconstruction must be given by the substrate consistent with the LEED results reported by Fan and Ignatiev [5].

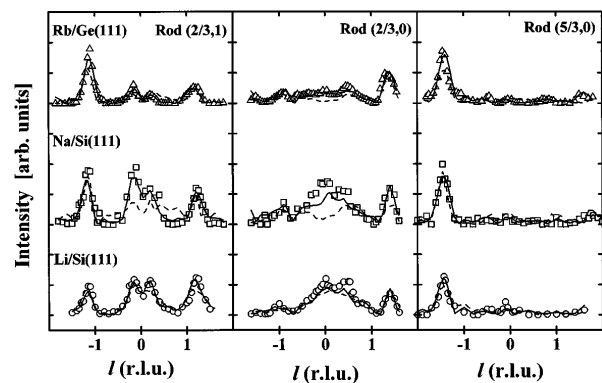


FIG. 2. X-ray structure factor intensities of six fractional-order rods of Si(111)- (3×1) -Li, Si(111)- (3×1) -Na, and Ge(111)- (3×1) -Rb, respectively, as a function of the momentum transfer l in the direction normal to the surface. The full line corresponds to the best fits without including the alkali metal atoms. The dashed line corresponds to the best fits with including the alkali metal atoms in 560560 position, in split positions (50% 560560 and 50% 650650), and 650650 position for Li/Si(111), Na/Si(111), and Rb/Ge(111), respectively.

Since the x-ray scattering cross section is proportional to the atomic number, we can safely neglect the scattering from the metal overlayer in the case of Li and concentrate on determining the substrate reconstruction. The strong intensity variation along the fractional-order rods indicates large subsurface relaxations extending over several atomic layers. First we tried the Seiwatz (500500) and the extended Pandey (567567) model to fit the SXRD data. Attempts to refine these models using a least-squares fitting routine, and allowing the atoms to relax in the mirror plane directions, failed to reproduce the data. The insertion of a six-membered ring into the sequence of the Seiwatz model dramatically improved the fits. Using a scale factor, refining the atomic positions in the fivefold and sixfold ring and allowing the next substrate layer to relax, gave $\chi^2 = 4.0$. The model is shown in Fig. 1(c) and can be labeled as a 560560 model. To check the correctness of the model it was then tested against the LEED data. Using it as a starting model, the full-dynamical analysis of the LEED data gave an acceptable agreement with an R factor of 0.38 with a flat surface layer. The structural parameters were then repiped as a trial model into the SXRD analysis. By including horizontal and vertical displacements down to the fourth substrate layer in the refinement, the χ^2 of the fractional-order data dropped to 1.8. Because of the large relaxation in the deeper layers, multiple local minima exist in the least-squares analysis, and it is very important to combine the SXRD and LEED analysis. In the SXRD analysis the relaxations of deeper substrate layers were constrained by a Keating calculation [19] to account for the elastic strain, while the positions of the topmost atoms were completely unconstrained. The height difference between the fivefold and sixfold ring

is only $0.15 \pm 0.09 \text{ \AA}$. With these new optimized geometrical parameters the LEED data were reanalyzed, giving $R_P = 0.36$ with an excellent agreement between the positions of the atoms derived by the SXRD and LEED analysis as seen in Table I. Just scaling these atomic coordinates to Ge, the LEED data of the Ge(111)-(3 × 1)-Li surface could be fitted as well. It is very unlikely that both Ge(111)-(3 × 1) and Si(111)-(3 × 1) produce coincident local minima in the R_P factor, so this strongly supports the assumption that we have now found the true surface structure. DFT calculations were performed for the models depicted in Fig. 1. Consistent with Erwin's calculation [10], the 500500 and 567567 models are energetically almost degenerated. However, the 560560 model is 0.4 eV more stable than these models. The optimum parameters (cf. Table I) compare well with those from LEED and SXRD. The model is further supported by the analysis of the Si(111)-(3 × 1)-Na and Ge(111)-(3 × 1)-Rb x-ray data. The Si(111)-(3 × 1)-Na x-ray fractional-order data can also be reproduced by adjusting only a scaling factor, but without including the metal atoms ($\chi^2 = 4.5$). By optimization of the structural parameters the χ^2 for the twelve fractional-order rods dropped to 2.4. The positions of the substrate atoms are, within $\sim 0.1 \text{ \AA}$, identical to the positions determined for the Si(111)-(3 × 1)-Li structure. A subset of the calculated rods is shown in Fig. 2. The 560560 model can also reproduce the Ge(111)-(3 × 1)-Rb x-ray data. The least-squares refinement gave a χ^2 of 3.2 including both the in-plane data set as well as the 16 fractional-order rods, as shown in Fig. 2 for a subset of the rods. The structure is very similar to the Si(111)-(3 × 1)-Li and Si(111)-(3 × 1)-Na structures. On scaling the Si structure to Ge, we find that the model is, to within $\sim 0.2 \text{ \AA}$, the same.

The characteristics of the (3 × 1) structure can be described as follows: The substrate reconstruction consists of consecutive five-member and six-member rings separated by empty channels. The atoms labeled 3 in Fig. 1(c) exhibit a planar configuration within 0.15 \AA which indicates rehybridization from sp^3 to sp^2 . Hence, the dan-

gling bond of atom 3 is empty. Atom 4 adopts bonding configuration with a fully occupied dangling bond. The bond lengths from atom 3 to 2 and from atom 3 to 4 are about 8% shorter than the bulk bond length, and the bond angles are around 120° , both consistent with a sp^2 rehybridization. The bond lengths for atom 4 are slightly longer than the bulk bond length. Altogether, there appears to be a flow of electronic charge from atom 3 to atom 4, thereby reducing the number of dangling bonds by 2 per (3 × 1) surface unit cell. This is supported by the DFT calculations. The only dangling bond left on the surface is located on atom 1. The role of the alkali metal is that of a donor which passivates the dangling bond, so that no unsaturated bonds remain.

The absolute coverage of the alkali metals is known to be 0.3 monolayer [9,20]. As noted above, both LEED and the fractional rods as measured by SXRD are insensitive to the alkali atoms. This is partly due to the large subsurface relaxations that dominate the SXRD rods. However, the model without the alkali atoms cannot fit the crystal truncation rods (CTR) [21], in particularly not for Ge(111)-(3 × 1)-Rb as shown in Fig. 3. This discrepancy can be resolved by inspecting the 560560 model. The distance between atom 2 and atom 6 is within $\sim 0.1 \text{ \AA}$ identical to the distance between atom 3 and atom 6; see Fig. 1(c). Hence, the bonding configuration can equally well be 650650 instead of 560560 as shown in Fig. 1(d). This has important consequences for the location of the alkali atom. In the 560560 model it would bind to atom 1, but in the 650650 model it would bind to atom 4. The structural analysis described above cannot distinguish between these two models, as they are not sensitive to the alkali atoms. However, including an alkali atom in the 650650 model for Ge(111)-(3 × 1)-Rb and refining on both CTR's and fractional-order rods dramatically improves the agreement as seen in Fig. 3. It is possible to refine the Rb atom to be $1.5 \pm 0.3 \text{ \AA}$ above surface. Similarly, the agreement to Si(111)-(3 × 1)-Na CTR's can be improved by including the Na atom, however, only with a model consisting of $\sim 50\%$ of the

TABLE I. Atomic coordinates of the Si(111)-(3 × 1)-Li structure in \AA as determined by SXRD, LEED, and DFT.

Atom	SXRD			LEED			DFT		
	X	Y	Z	X	Y	Z	X	Y	Z
1	1.16	0.00	2.35	0.96	0.00	2.18	0.89	0.00	2.42
2	2.29	1.92	2.26	2.35	1.92	2.31	2.27	1.92	2.30
3	4.32	1.92	2.35	4.48	1.92	2.29	4.59	1.92	2.30
4	5.68	0.00	2.32	5.75	0.00	2.33	5.98	0.00	2.39
5	0.33	0.00	0.09	0.27	0.00	0.02	0.16	0.00	0.10
6	3.55	1.92	0.00	3.66	1.92	0.00	3.41	1.92	0.00
7	6.72	0.00	0.18	6.68	0.00	0.00	6.64	0.00	0.08
8	1.26	1.92	-0.87	1.31	1.92	-0.84	1.16	1.92	-0.83
9	4.58	0.00	-0.94	4.74	0.00	-0.86	4.48	0.00	-0.84
10	7.91	1.92	-0.56	7.81	1.92	-0.71	7.84	1.92	-0.63

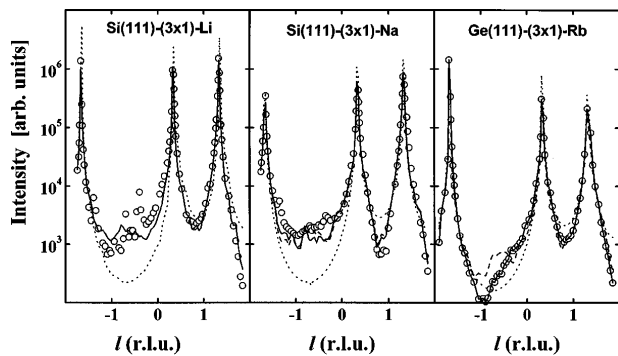


FIG. 3. The structure factor intensities of the (ten) crystal truncation rods of Si(111)-(3 × 1)-Li, Si(111)-(3 × 1)-Na, and Ge(111)-(3 × 1)-Rb, respectively, as a function of the momentum transfer l in the direction normal to the surface. The solid line corresponds to the best fits with including the alkali metal atoms in 560560 position, in split positions (50% 560560 and 50% 650650), and 650650 position for Li/Si(111), Na/Si(111), and Rb/Ge(111), respectively. The dashed line in the Rb/Ge(111) plot corresponds to the best fits without an inclusion of the Rb atoms. The dotted line corresponds to an ideal terminated surface.

560560 model and $\sim 50\%$ of the 650650 model. This suggests a degeneracy between the two models which could explain the difficulties in understanding the electronic properties of the Si(111)-(3 × 1)-Li system with only one Li adsorption site, whereas, the Li $1s$ core level spectrum has to be fitted with two components [9]. This is supported by the DFT calculations which show that the 560560 structure is only 20 meV energetically more favorable than the 650650 structure. A superordering of the sites into a 560650 structure could also explain the tendency for Si(111)-Ag to form a (6 × 1) structure [8]. The new structural model can also explain other experimental findings. For instance, the charge transfer from atom 3 to atom 4 transforms the otherwise metallic surface into a semiconducting one [6]. The double stripes observed in the filled state STM images and the single stripes in the empty state STM images can be reconciled by assigning the rows of empty states to atom 3 and the rows of filled states to atoms 1 and 4 [8].

In conclusion, by combining SXRD and LEED IV measurements with *ab initio* calculations a new structural model has been discovered for the alkali metal induced (3 × 1) reconstructions of Si(111) and Ge(111). The structural model is denoted as the 560560 or 650650 model, exhibiting alternating fivefold and sixfold rings. The structure is low-energy configuration with no dangling bonds, having two parallel substrate chains and

the adsorbate in the empty channel as a basic unit. The structure can probably be generalized beyond the present investigated adsorbate systems to explain the occurrence of (3 × 1) reconstructions for other adsorbates.

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Note added.—A model based on transmission electron diffraction data has just been published for the Si(111)-(3 × 1)-Ag structure showing a similar substrate reconstruction as presented in this paper [22].

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