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Dimer-chain model for the 7×7 and the 2×8 reconstructed surfaces of Si(111) and Ge(111)

Kunio Takayanagi and Yasumasa Tanishiro
Department of Physics, Tokyo Institute of Technology, Oh-okayama, Meguro-ku, Tokyo 152, Japan

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A dimer adatom stacking-fault model for the Si(111)-7×7 reconstructed surface structure is described as a network of walls and domains. The wall consists of a chain of dimers and the domain of adatom clusters and adatoms arranged locally in a 2×2 structure on a "1×1" surface lattice. It is shown that with a proper wall configuration (dimer chain), a new structure model for the Ge(111)-2×8 reconstructed surface can be made. The structure, which has four adatom clusters and three dimers in a unit cell with only four dangling bonds, is consistent with the scanning tunneling-microscopy image and electron-diffraction data. A dimer-chain structure which describes reconstructed structures of $n\times n$ with odd periodicity and $2\times m$ with even periodicity is presented.

I. INTRODUCTION

It is important to understand the reconstruction of surfaces; however, reconstructed structures are not easily analyzed at the atomic level. Si(111)-7×7 and Ge(111)-2×8 structures have long been subjects of dispute. For the 7×7 reconstruction of the Si(111) surface, theories proposed for the mechanism of reconstruction have included vacancies,[1] rippling,[2] adatoms,[3] adatom clusters,[4] and stacking faults.[5] Evidence that a 2×2 unit is a building block of the 7×7 structure has been produced from structural studies by LEED (low-energy electron diffraction),[6] RHEED (reflection high-energy electron diffraction),[7] STM (scanning tunneling microscopy),[3] and TED (transmission electron diffraction).[8–10] In previous papers,[9,10] we proposed a dimer adatom stacking-fault (DAS) structure model which is obtained by analyzing TED intensity. The model consists of 12 adatoms, a stacking-fault layer, and a dimer layer with a vacancy at the corner of the 7×7 unit cell (Fig. 9 in Ref. 10). Recently, a STM image of a stepped Si(111)-7×7 surface[11] has been reported which agrees with the DAS model. X-ray-diffraction intensity[12] is explained by the DAS structure, and detailed Rutherford-backscattering (RBS) spectra are also explicable when subsurface relaxation and softening of surface-atom vibration are properly taken into account.[13] The DAS structure, therefore, seems to represent a main configuration of the Si(111)-7×7 surface, except for minor corrections.

For the Ge(111)-2×8 structure, experimental evidence suggests that the Ge(111)-2×8 has a building block of the 2×2 unit[14–16] with atomic arrangements similar to Si(111)-7×7.[14,17] One confirmation of this is that the Ge(111)-7×7 structure grown on the Si(111)-7×7 surface and the Ge(111)-2×8 structure transformed by subsequent annealing produce similar STM images showing protrusions arranged locally in a 2×2 structure.[14] In LEED, the Ge(111)-7×7 shows intensities similar to the Si(111)-7×7.[17] Other supplemental evidence supporting the structural similarity between Ge(111)-2×8 and Si(111)-7×7 is found in RHEED and LEED studies: Ge(111)-2×8 surface changes to 7×7 and 5×5 structures by deposition of Sn,[18] and the Si(111)-7×7 surface changes to a 5×5 structure by deposition of Ge.[19–21] These 7×7 and 5×5 structures present RHEED and LEED intensity distributions similar to the Si(111)-7×7.[18,20,22] Ino *et al.* have noticed the similarity and proposed models of the 2×8, 7×7, and 5×5 structures[23] based on the rippling of surface atoms.[24] Becker *et al.*[14] considered adatoms for the protrusion found in their STM image of a Ge(111)-2×8 structure and Phaneuf and Webb[25] assumed adatoms to explain a higher-temperature phase observed in LEED. Kanamori[26] recently discussed the stability of 7×7, 5×5, and 2×8 structures with use of a lattice-gas model, assuming identical adatoms (adatom clusters) to be arranged locally in a 2×2 structure; however, it is not clear whether the Ge(111)-2×8 and Si(111)-7×7 surfaces are constructed by identical adatoms. The 7×7 structure derived from the simple lattice-gas model is not consistent with the DAS structure.[27]

The similarity of the 7×7 and 2×8 structures indicates that they are stabilized by a common mechanism. The driving mechanism which stabilizes the 7×7 reconstruction of the DAS structure is the reduction in the number of dangling bonds; this number is only 19, or 39% of the 49 dangling bonds of the unreconstructed surface.[10] Yamaguchi has confirmed by Keating calculation that the DAS structure is stabilized due to reduction in the number of dangling bonds, although unusual coordination around the adatoms gives rise to large strain energy.[28] Since this reduction in the number of dangling bonds is caused by the adatoms (including atoms in the stacking-fault layer) and dimers, the arrangement of these factors in the 2×8 structure is also considered to minimize the number of dangling bonds, or the surface energy.

In this paper we describe a dimer-chain model which systematically explains $n\times n$ (of odd periodicity) and $2\times m$ (of even periodicity) reconstructed structures. First, we redefine the construction of the DAS structure and describe it as walls and domains: a wall consists of a chain of dimers and a domain contains six adatom clusters and three adatoms arranged locally in 2×2. In Sec. III stable wall configurations are described and in Sec. IV a possible 2×8 structure for a stable wall arrangement is given. The 2×8 structure model has only four dangling bonds per unit cell, 25% of the bulk exposed surface. In Sec. V the structures 7×7 and 2×8 consisting of walls and domains are discussed. Structural details are described here and their stability will be discussed separately.[29]

II. WALL CONFIGURATION FOR DAS STRUCTURE

Figure 1 shows a top view of the DAS model (also see Fig. 9 in Ref. 10). Open circles and solid circles indicate atoms in the reconstructed and the underlying layers, respectively (larger circles are closer to the vacuum). A new concept is introduced wherein the DAS structure is constructed by walls and domains as shown in Fig. 2: a domain corresponds to a triangular subcell of the 7×7 unit cell and a wall corresponds to an array of dimers at the sides of a triangular subcell. We consider adatom clusters (open or solid triangles in Fig. 2) and adatoms (dots in Fig. 2) in each domain. An adatom cluster, *P*, represented by an open triangle, consists of one adatom at an *A* site bonded with three atoms at *B* sites in the stacking-fault layer in the DAS model; these appear as four atoms in each shaded triangle in the right triangular subunit in Fig. 1. An adatom cluster, *N*, represented by a solid triangle in Fig. 2, consists of one adatom at an *A* site and three atoms at *C* sites. The adatoms shown by dots (atoms in the stacking-fault layer in the DAS model) are at the center of three adatom clusters arranged in a triangle. These adatom clusters and adatoms are on a "1×1" surface layer (the dimer layer in the DAS model), in which atoms are located at *a* sites, except for those forming dimers at the wall. Where the three walls intersect, one atom in the "1×1" layer becomes vacant as shown by open circles in Fig. 2. Since the wall is constructed by an array of dimers, we call the structure a dimer-chain model. It is noteworthy that a series of reconstructed structures having $n\times n$ of odd periodicity are described by dimer-chain structures like that in Fig. 2.

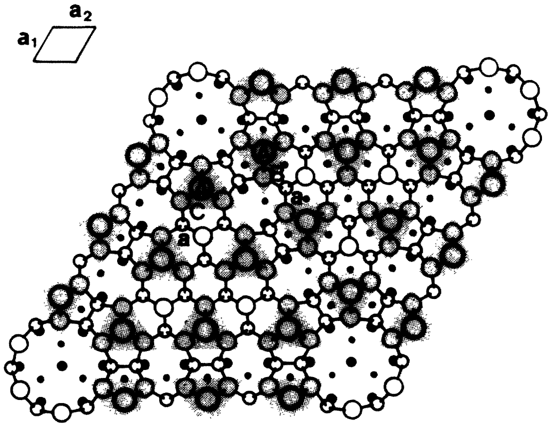

FIG. 1. Top view of the DAS structure. The 7×7 unit cell is divided into two triangular subcells. On each side of the subcells dimers are formed. Shaded triangles in the right and left triangular subcell represent adatom clusters of types *P* and *N*, respectively.

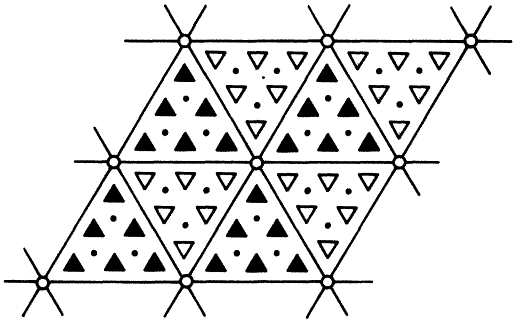

FIG. 2. Wall and domain configuration of the 7×7 structure. Open and solid triangles represent adatom clusters of *P* and *N* types, respectively, and dots represent adatoms. Each solid line indicates a dimer chain of a type-I wall. Open circles at the intersection of the walls represent vacancies.

We compare the stability of the 7×7 structure with a 2×2 structure shown in Fig. 3, in which adatoms are located at *A* sites on the bulk exposed 1×1 surface composed of atoms at *B* sites. Alternatively, this 2×2 structure is constructed by adatom clusters and adatoms arranged in a 2×2 structure above *a* sites of the "1×1" surface, corresponding to an $n\times n$ dimer-chain structure of infinite *n*. In the 2×2 structure, one adatom occupies three dangling bonds of the "1×1" layer and an adatom cluster occupies nine dangling bonds. For the 7×7 structure, in addition, two dangling bonds in the "1×1" layer are eliminated by each dimerization at the wall. Since no large strains are associated with the dimerization,[28,29] the wall (dimer chain) formation is the key mechanism stabilizing the 7×7 reconstruction.

III. STABLE WALL CONFIGURATIONS

Walls which form dimer chains are types I, II, and III as shown in Figs. 4(a), 4(b), and 4(c), respectively. They

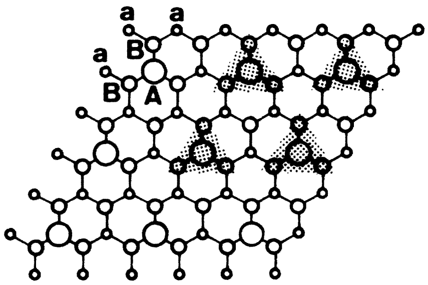

FIG. 3. 2×2 adatom structure: The largest circles are adatoms at *A* sites, which are bonded with atoms (medium circles) at *B* sites in the bulk exposed 1×1 surface. Note that this is an $n\times n$ dimer-chain structure of infinite *n*, which is constructed by adatom clusters (shaded triangles) and adatoms on the "1×1" surface of atoms at *a* sites (the smallest circles).

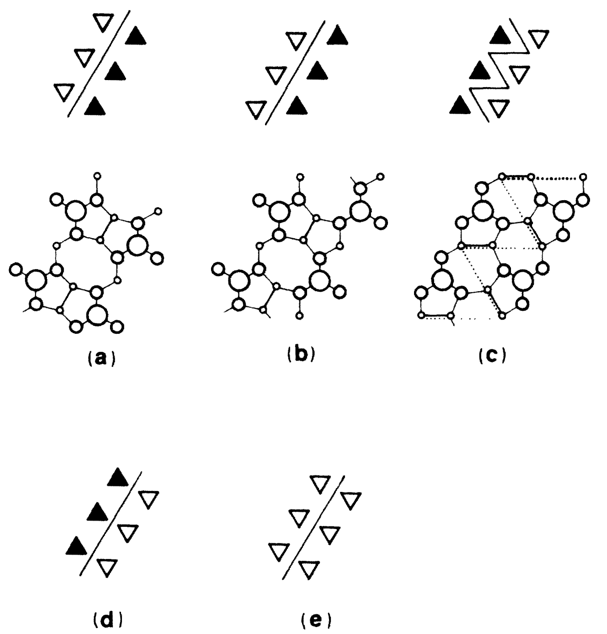

FIG. 4. Walls of types I, II, and III in (a), (b), and (c), respectively, which form dimer chains along the solid lines as shown in the lower portion. Open and solid triangles represent adatom clusters of *P* and *N* types, respectively. Note the zigzag dimer chain and alternation of five- and seven-member rings along wall III.

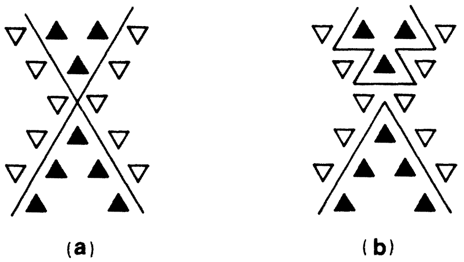

FIG. 6. Split of a wall intersection into walls of types II and III after dimerization.

accommodate different arrangements of type-*P* and -*N* adatom clusters. As will be shown in a later paper,[29] strain energies of the three types of walls associated with each dimerization were estimated by Keating calculation to be at a ratio of 1:1.6:3. The type-I wall of the lowest strain energy is found in the 7×7 structure. The type-III wall of the highest strain energy has an interesting atomic arrangement as shown in the lower portion of Fig. 4(c): a zigzag chain of dimers (indicated by dotted lines) with a five-member ring and a seven-member ring formed alternately along the chain. Other wall configurations such as in Figs. 4(d) and 4(e) do not form dimer chains, resulting in higher energy. Provided the walls of types I—III are allowed, the following rule for wall arrangements applies, taking into account the "frustration" in the location of adatom clusters of types *P* and *N*: (1) A wall can turn only with an acute (60°) angle as shown in Fig. 5(a). (2) Three straight walls can intersect at one point as shown in Fig. 5(b) with a vacancy. (3) Types I and III or types II and III are formed alternately, since parallel wall arrangement results in a wall configuration in Fig. 4(d) with higher energy. It is worth noting that wall arrangements such as parallel walls, zigzag walls with an obtuse (120°) angle, and intersection of two walls are not stable; for example, intersecting walls in Fig. 6(a) are rearranged by dimerization into two walls of types II and III as shown in Fig. 6(b).

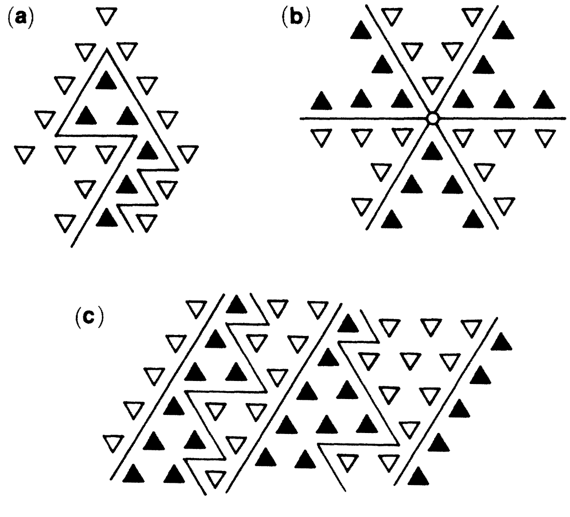

FIG. 5. Stable wall arrangements: (a) wall turning with an acute (60°) angle, (b) three walls intersecting at a vacancy, and (c) alternation of type-I and -III walls. Adatoms (represented by dots in Fig. 2) are not shown.

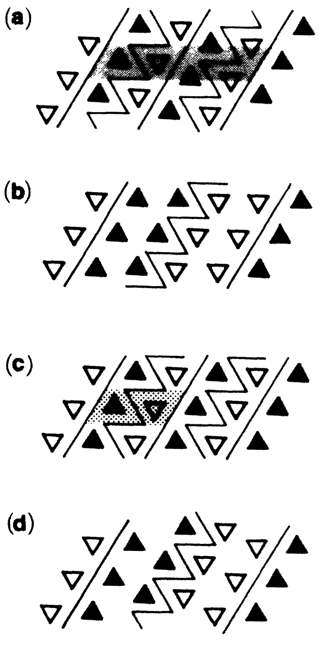

FIG. 7. (a) Wall arrangement for a 2×8 structure. Solid lines indicate walls (dimer chain) of types I and III, and shaded area indicates the 2×8 unit cell. (b), (c), and (d) show other arrangements of walls resulting in different adatom cluster arrangements. Note that (c) gives a 2×4 structure. Adatoms (represented by dots in Fig. 2) are not shown in (b) and (d).

IV. STRUCTURE OF Ge(111)-2×8

A. Structure model

Following the rule described in Sec. III, a wall arrangement for the Ge(111)-2×8 structure is deduced as shown in Fig. 7(a). The structure is constructed by alternating walls of types I and III. In the 2×8 unit cell indicated by a shaded area, four adatom clusters are included. Figure 8(a) shows an atomic arrangement of the four adatom clusters sitting on a "1×1" surface before dimerization, where the smallest open circles indicate atoms at a sites in the "1×1" plane. On the zigzag dashed line, each atom in the "1×1" plane has one dangling bond. Therefore, if a pair of atoms, A and B, form a dimer, a chain of dimers, CD, EF, etc., is formed along the zigzag line to make up a type-III wall. Figures 8(b) and 8(c) show structures after such dimerization; they differ in the order of pairing for dimerization. The ordering can be switched from one to the other through a defect in the atom marked X in Fig. 8(c).

For the other wall arrangements, structures having a 2×8 unit cell are obtained as shown in Figs. 7(b)—7(d). However, these structures do not agree with LEED and RHEED observations as described below.

It is noticed that an alternating arrangement of walls II and III in Fig. 7(c) results in a 2×4 structure. This structure, however, has a slightly higher energy than the 2×8 structure, since the type-II wall in the 2×4 structure has higher strain energy than the type-I wall.[29] It is easily proved that the 2×8 structure in Fig. 7(a) has the lowest energy among $2\times m$ structures of even periodicity ($m = 4,8,\ldots$), which are constructed by alternating straight and zigzag wall arrangements.[29]

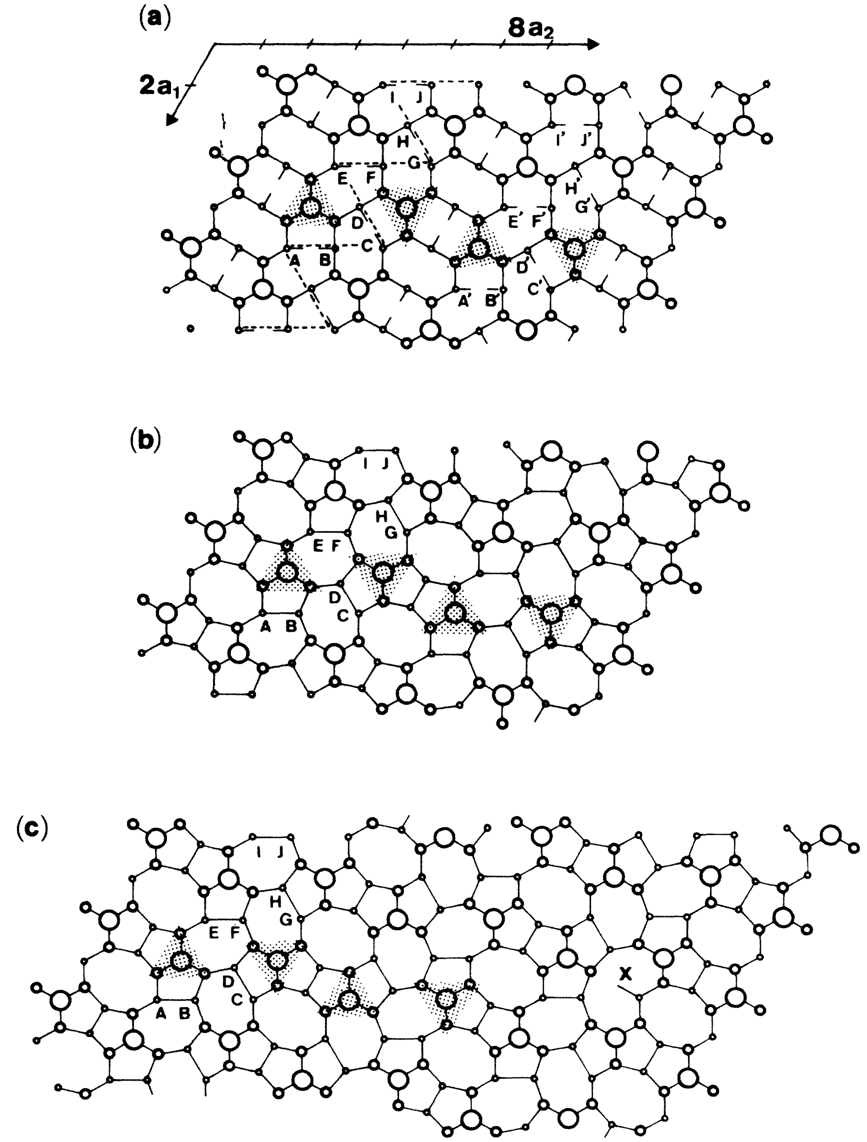

FIG. 8. Atomic structures for the wall arrangement in Fig. 7(a): (a) before and (b) and (c) after dimerization. Note that they have two-dimensional symmetry of $C2mm$, Cm, and $P2gg$, respectively.

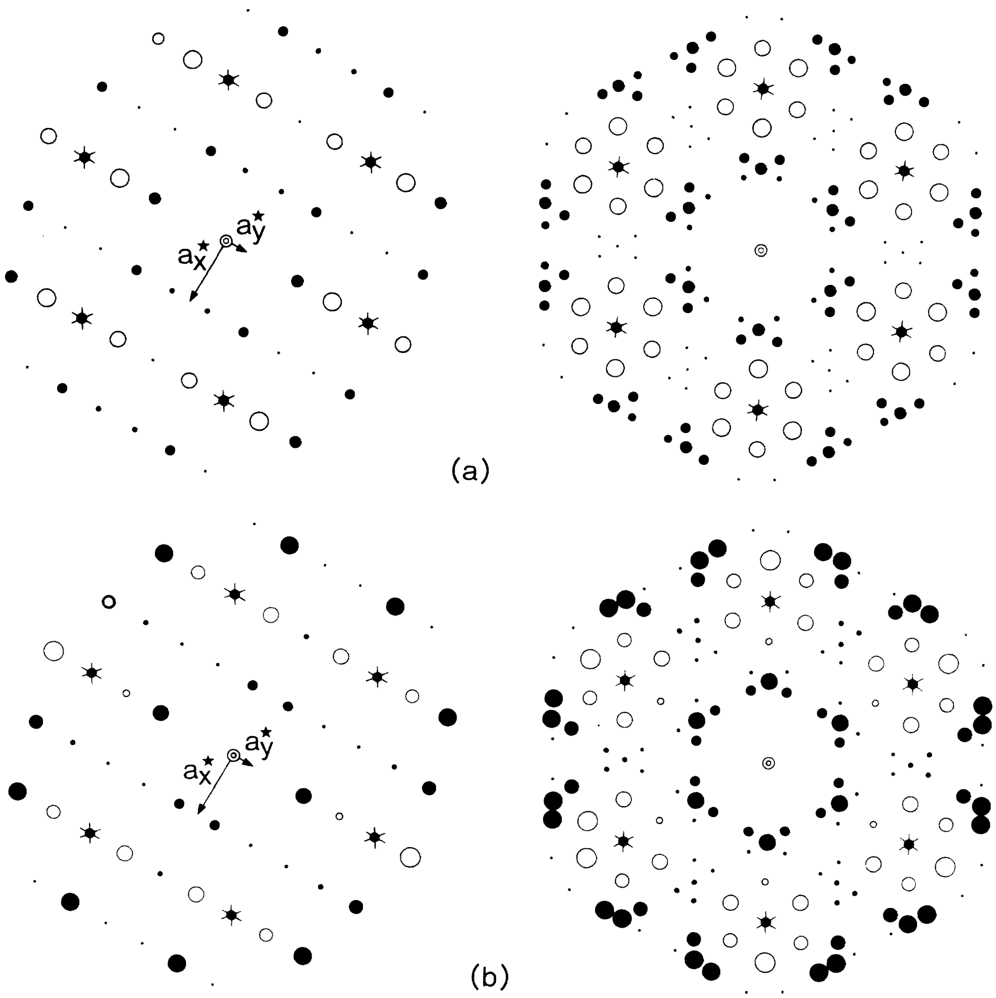

FIG. 9. (a) Diffraction pattern for the structure in Fig. 8(a) and a superimposition from three domains, and (b) the same for the structure in Fig. 8(b). Open circles are $\{0\,\frac{1}{4}\}$-type reflections and the circle size indicates relative intensity. The intensity of higher-order reflections is overestimated, since the scattering-angle dependence of the atomic-scattering factor is neglected.

B. Test of models by diffraction data

Yang and Jona[15] and Chadi and Chiang[30] deduced that the Ge(111)-2×8 structure has a centered lattice from the systematic absence of the diffraction spots in LEED and RHEED patterns,[31–33] the extinction rule. We test whether the 2×8 structures in Figs. 8(a)–8(c) agree with the observed extinction rule, which generally restricts symmetry of a structure. We choose a rectangular unit cell of $a_x=2a_1$ and $a_y=4a_1+8a_2$, where a_1 and a_2 are the unit-cell vectors for the 1×1 surface. The above structures, then, have symmetries (two dimensional) of $C2mm$, Cm, and $P2gg$, respectively.[34] The (hk) reflections of $C2mm$ and Cm structures are absent for $h+k=\text{odd}$, to give the diffraction patterns shown in Figs. 9(a) and 9(b), respectively, while those of $P2gg$ are absent for $h=0$, $k=\text{odd}$ and $h=\text{odd}$, $k=0$. It is noted in Fig. 9 that $\{0\,\frac{1}{4}\}$-type spots (open circles) appear. These spots are not recognized in the LEED pattern,[31,32] but are seen clearly in the RHEED pattern (Fig. 1 in Ref. 33), where they were interpreted by Ichikawa and Ino as having been the result of double diffraction.[33] Phaneuf and Webb[25] have recently observed weak $(0\,\frac{1}{4})$ and $(0\,\frac{3}{4})$ reflections in their LEED pattern, which indicates that (hk) reflections of $h+k=\text{even}$ are allowed.[35] Therefore, centered 2×8 structures in Figs. 8(a) and 8(b) coincide with the extinction of the diffraction data, while a primitive structure in Fig. 8(c), which has the glide plane, does not. Diffraction intensity calculated for a stable $c(2\times8)$ dimer-chain structure in Fig. 8(b), which gives rise to

TABLE I. The number of dangling bonds (NDB) in the unit cell for the present dimer-chain model and the fraction of dangling bonds (FNDB). Density of the surface layer (DSL) is for the adatom clusters and adatoms on the "1×1" surface.

	2×2	7×7	5×5	2×8	2×4
NDB	2	19	9	4	2
FNDB	0.50	0.39	0.36	0.25	0.25
DSL	1.00	1.08	1.00	1.00	1.00

weak $(0\,\frac{1}{4})$ and $(0\,\frac{3}{4})$ reflections in comparison with the $\{0\,\frac{1}{2}\}$- and $\{0\,\frac{1}{8}\}$-type reflections as shown in Fig. 9(b), does agree with the diffraction data, although the calculated intensity has to be compared with TED data at the normal incidence.

V. SUMMARY AND DISCUSSION

The DAS structure for Si(111)-7×7 is shown to be constructed by a network of type-I walls. The walls are introduced to reduce the number of dangling bonds caused by dimerization. The 2×8 structure is constructed by alternating walls of types I and III to result in the smallest number of dangling bonds. The centered 2×8 structure with adatom clusters arranged in a 2×2 structure is consistent with the STM image and the extinction of the diffraction data. Reconstructed structures of $n\times n$ and $2\times m$, respectively, of odd and even periodicities, are described by dimer-chain structures composed of domain and walls of types I—III. Table I lists a fractional number of dangling bonds (FNDB) and the density of the surface layers (DSL) for the 2×2, 2×8, 7×7, and 5×5 structures. The fractional number of dangling bonds for the 2×8 structure is extremely low, 25% of the bulk exposed surface. The density of the surface layer including the adatoms, adatom clusters, and vacancies is around 1.

It is suggested that Sn-stabilized 7×7 and 5×5 structures on Ge(111) (Ref. 18), Ge(111)-7×7 grown on Si(111) (Ref. 14), and 5×5-Ge structure grown on Si(111) (Refs. 19 and 36) are strain sensitive. Ino *et al.*[23] supposed that their rippled-surface model was appropriate to explain the structural changes caused by deposition of Sn on Ge(111) and Ge on Si(111). McRae *et al.*[22] proposed a triangle-dimer stacking-fault (TDSF) model for Si(111)-5×5-Ge in analogy with Si(111)-7×7 from the LEED intensity analysis. McRae and Malic[36] suggested that the stability of the TDSF model is dependent on lateral compressive stress consistent with the experiment, since the backbonding of surface atoms to atoms directly below them causes lateral compression of the two outermost double layers. For the dimer-chain model, the stability of the $n\times n$ and $2\times m$ structures depends on the strain energy of the walls and of adatom clusters relative to the bond-breaking energy[29] which, in turn, depend on the force constants and lattice parameters of deposits.

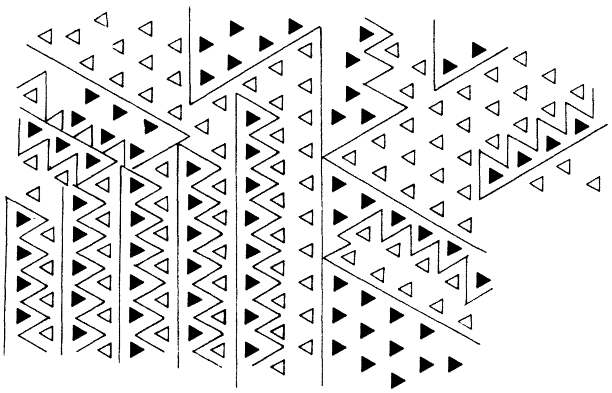

FIG. 10. Wall arrangement for a mixture of 2×2, 2×4, and 2×8 structures. Straight and zigzag lines are type-I and -III walls, respectively. Adatoms (represented by dots in Fig. 2) are not shown.

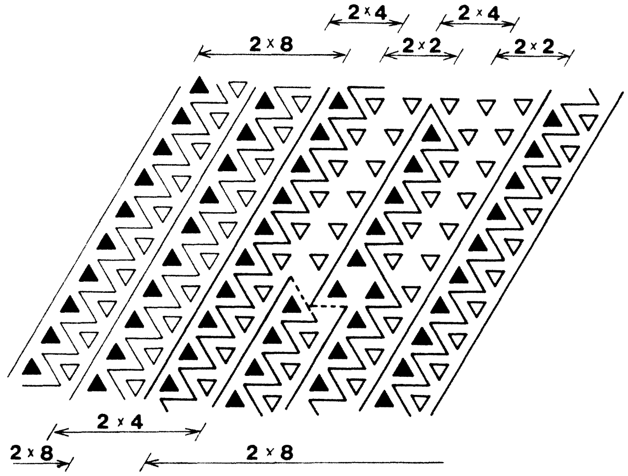

FIG. 11. Wall arrangement of a disordered 2×8 structure. Adatoms are not shown.

An arrangement of protrusions in a recent STM image of the Ge(111)-2×8 surface, (Fig. 3 in Ref. 14) is a mixture of 2×2, 2×4, and 2×8 structures. We cannot judge from the image whether the arrangement is a stable one or not and whether a similar arrangement extends over the entire surface area or is only local. The arrangement is reproduced partly by the present model as shown in Fig. 10. Walls of types I and III are shown by solid lines and the adatom clusters of P and N types are shown by triangles which are placed at positions of the protrusions in the STM image. For the 2×8 domain in the lower left portion of Fig. 10, a pair of the type-I and -III walls is formed like a hairpin. They are assumed to have grown from the lower part of the figure and to have transformed a 2×2 structure to a 2×8 structure. Since the type-II wall has slightly larger strain energy than the type-I wall, domains of the 2×4 structure in Fig. 7(c) seem to be introduced in the 2×8 domain by slight thermal excitation. Such hairpin-like and striped-wall arrangements of dimer chains (Fig. 11) might correspond to a floating phase of the 2×8 structure as pointed out first by Kanamori[26] for the higher-temperature phase of the Ge(111) surface.[25,37] The structure, which gives diffuse reflection around positions of $\frac{1}{8}$- and $\frac{1}{2}$-order spots, was once interpreted as being due to disorder of the 2×2 building block[37] and it has recently been suggested that it is due to a honeycomb wall arrangement from detailed LEED study of the diffuse intensity.[25] The present postulation for the floating of the 2×8 walls should be further investigated theoretically and experimentally.

ACKNOWLEDGMENTS

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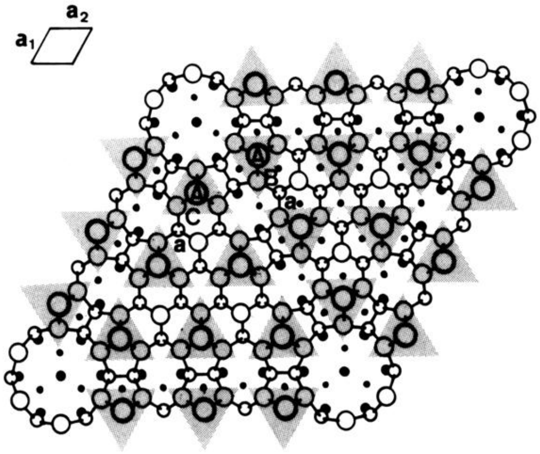

FIG. 1. Top view of the DAS structure. The 7×7 unit cell is divided into two triangular subcells. On each side of the subcells dimers are formed. Shaded triangles in the right and left triangular subcell represent adatom clusters of types *P* and *N*, respectively.

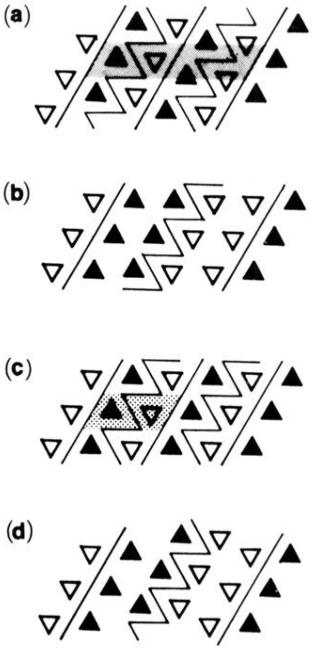

FIG. 7. (a) Wall arrangement for a 2×8 structure. Solid lines indicate walls (dimer chain) of types I and III, and shaded area indicates the 2×8 unit cell. (b), (c), and (d) show other arrangements of walls resulting in different adatom cluster arrangements. Note that (c) gives a 2×4 structure. Adatoms (represented by dots in Fig. 2) are not shown in (b) and (d).