# New $c$-2×8 unit cell for the Ge(111) surface

D. J. Chadi and C. Chiang
*Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, California 94304*
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The smallest unit cell consistent with electron-diffraction patterns of the 8th-order reconstructed Ge(111) surface is shown to be a $c$-2×8 cell and not the commonly assumed 2×8 cell. A structural model consistent with the observed electron-diffraction data is proposed.

The atomic arrangement on the clean and annealed Ge(111) surface is commonly believed to have a 2×8 unit cell at room temperature.[1] The reconstructed surface, denoted by Ge(111)8 in the past,[2,3] has an unusual low-energy-electron-diffraction (LEED) pattern, shown in Fig. 1(a), with many $\frac{1}{8}$-order beams missing. From simple analyses of LEED data[1,4] surface unit cells with 2×8, 4×8, and 8×8 periodicities have been suggested. All three structures have reciprocal unit meshes which reproduce all the observed LEED beams, but in addition, each one has an appreciable number of extra points which do not correspond to any diffraction spot.

Palmberg and Peria[1] suggested that among the structures consistent with the observed LEED patterns the 2×8 structure was optimal in the sense that it had a minimum number of extra points on the unit mesh. The vanishing of the surface structure factor was assumed to explain[1,4] the absence of these extra spots in LEED. For 4×8 and 8×8 unit cells the nonobservation in LEED of much larger sets of points of the reciprocal mesh would have to be similarly explained. As a result, the 2×8 unit cell has generally been assumed to be the most appropriate one for the Ge(111)8 surface.

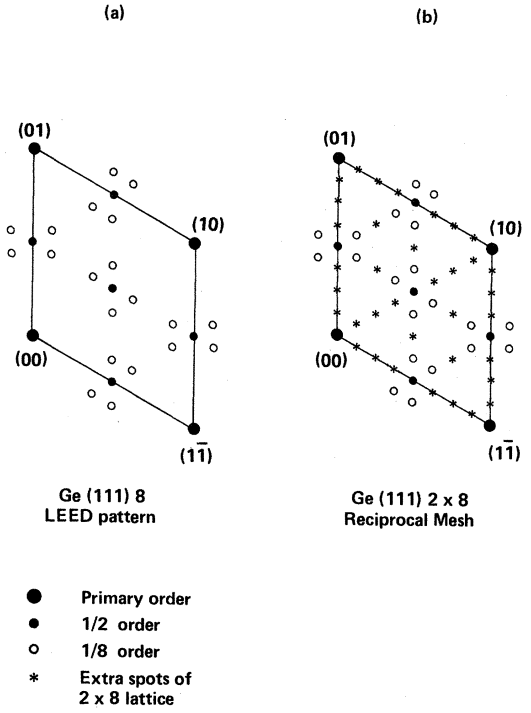


FIG. 1. The LEED pattern of the Ge(111)8 surface is shown in (a) for comparison to the reciprocal mesh of the 2×8 surface in (b).

Applying the same criterion as Palmberg and Peria, we find, however, that the optimal unit cell for Ge(111)8 is *centered* 2×8 and not 2×8. The absence of most $\frac{1}{8}$-order spots in LEED, which require the assumption of structure-factor cancellations for $(2n)\times 8$ surfaces, occurs naturally for the $c$-2×8 cell. Recent reflection-high-energy-electron-diffraction (RHEED) measurements,[5] as shown below, provide even stronger evidence than LEED for the $c$-2×8 cell.

The intepretation of the Ge(111)8 electron-diffraction pattern is complicated by the presence of domains oriented along the three different, but equivalent, directions at the surface. This makes it difficult to determine experimentally which domains are involved in producing a given fractional-order diffraction spot. It is not presently clear whether a one-domain region, which would simplify the LEED analysis and provide unambiguous information on the unit-cell dimension, can be easily created on the annealed Ge(111) surface.

The simplest structure with $\frac{1}{8}$-order beams is the one with a 1×8 unit cell. This structure can be ruled out, however, because it does not account for all the beams observed in LEED measurements. For the twice larger 2×8 cell, the reciprocal mesh as shown in Fig. 1(b) contains too many points when compared to the Ge(111)8 LEED pattern in Fig. 1(a). A much better correspondence between the reciprocal mesh and the LEED pattern occurs for a $c$-2×8 structure. The principal lattice vectors $\vec{R}=(R_x,R_y)$ of this structure, for one of the three possible domains

 

at the surface, are given by

$$\vec{R}_1 = (2, 0)a, \quad \vec{R}_2 = (1, 2\sqrt{3})a, \tag{1}$$

where $a$ is the hexagonal lattice constant.

The principal reciprocal-lattice vectors are given by

$$\vec{G}_1 = (\tfrac{1}{2}, \tfrac{1}{4}\sqrt{3})2\pi/a, \quad \vec{G}_2 = (0, \tfrac{1}{2}\sqrt{3})2\pi/a. \tag{2}$$

The superposition of the reciprocal meshes of the $c$-$2\times 8$ structure, assuming the presence of three equivalent domains at the surface, is shown in Fig. 2(a); the one-domain pattern is given in Fig. 2(b). Comparison with Fig. 1(a) shows that the $c$-$2\times 8$ unit cell reproduces all the LEED spots and that it has additional $\frac{1}{4}$-order points on the unit mesh corresponding to $\vec{G}_2$ and other related reciprocal-lattice vectors (e.g., $\frac{3}{4}$-order, etc.). These spots are apparently too weak to be seen in LEED. Clear indication for the presence of the $\frac{1}{4}$-order beams has, however, been obtained in recent RHEED measurements,[5] where it has been established that they appear and disappear simultaneously with the $\frac{1}{8}$-order spots as a function of temperature. The $\frac{1}{4}$-order spots in RHEED were interpreted, however, as arising from double diffraction.

The intensity of the $\frac{1}{4}$-order spots will be weak if the magnitude of the surface structure factor $S(\vec{G})$ corresponding to these points is small. The requirement that $S(\vec{G})$ should be nearly zero for the $\frac{1}{4}$-order spots leads to correlations between the atomic displacements at the surface. Several classes of solutions to the condition $S(\vec{G}) = 0$ can be obtained. The only solution which does not involve any assumptions on the magnitudes of the atomic motions is given by

$$\Delta\vec{r}_i = \Delta\vec{r}_{i+4}, \quad i = 1, 2, 3, 4 \tag{3}$$

where $\vec{r} = (r_x, r_y, r_z)$ and where the ordering of atoms is shown in Fig. 3.

Equation (3) provides only a partial description of the $c$-$2\times 8$ surface reconstruction. Additional information on the details of the surface rearrangement can be obtained only by relying on the

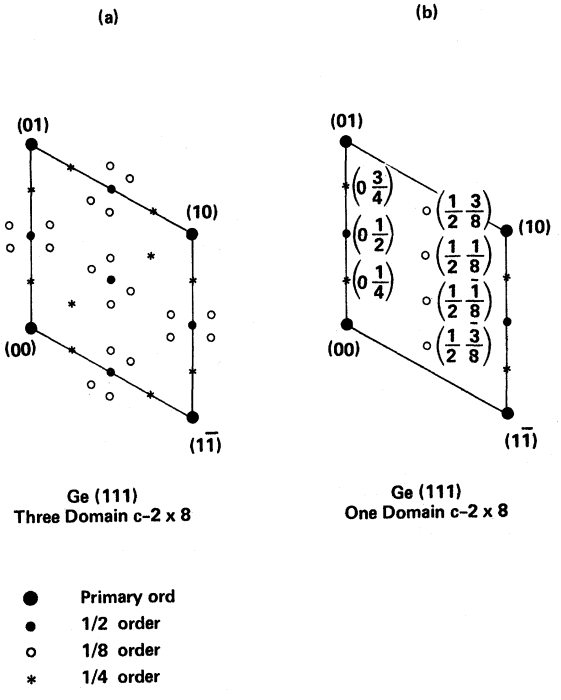


FIG. 2. The reciprocal mesh of the $c$-$2\times 8$ unit cell for a three-domain surface is shown in (a) and for a one-domain surface in (b).

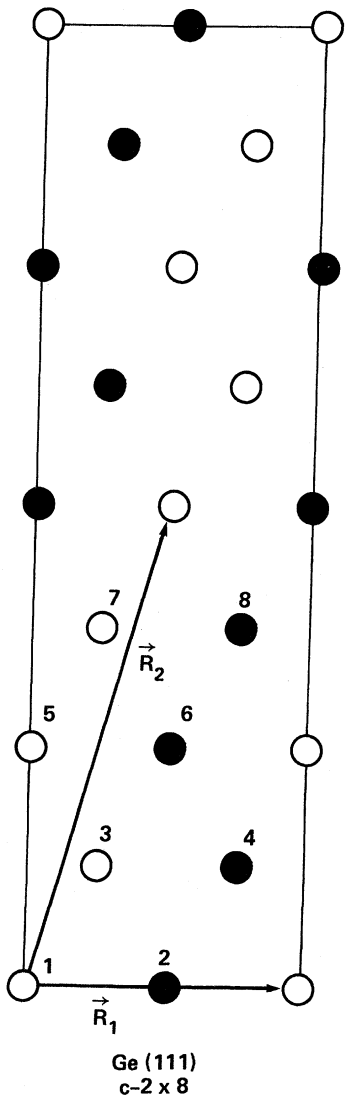


FIG. 3. The $2\times 8$ and $c$-$2\times 8$ unit cells of the Ge(111) surface. For the buckled model, the raised and lowered atoms are shown as open and dark circles, respectively.

results of surface sensitive experiments. There have been several experimental studies[6-12] of the Ge(111)8 surface. Photoemission studies[9,10] show the Ge(111)8 and 2×1 reconstructed surfaces to be similar, with maxima in the surface-band density at 0.7 and 0.6 eV below the top of the valence band, respectively, and with practically the same[9] value for the density of states. This has led to the suggestion that the Ge(111)8 and 2×1 surfaces involve similar types of reconstruction.[9] The relatively low temperature of 240°C, at which a reversible 2×8 to 1×1 transition occurs, and the ease with which the $\frac{1}{8}$-order LEED spots are removed by the addition of less than 0.1 monolayer of impurity atoms[6,11,12] also suggest that the Ge(111)8 reconstruction corresponds to a "smooth" surface with no vacancies[13] or other sharp structure.

If the $c$-2×8 and 2×1 reconstructions are assumed to be similar in character, involving a raising and lowering of surface atoms, then Eq. (3) leads to a single type of structure which is shown in Fig. 3. This surface and the 2×1 surface are alike in that both involve a stacking together of neutral rows of atoms. In both structures the nearest-neighbor environment of every "up" atom consists of four lowered and two other up atoms (and conversely for the lowered atoms). Assuming a similar charge transfer between up and down atoms, the two surface Madelung energies are found to be very nearly equal with the 2×1 surface being slightly more favorable.[14]

An interesting consequence of a $c$-2×8 unit cell is that the equivalence between atomic displacements specified by Eq. (3) cannot be exact but must be only approximately correct. The reason for this is that the atom pairs in Eq. (3) with correlated displacement are not in identical environments. For the buckled model, for example, the arrangement of up and down atoms around atoms 1 and 5 [which from Eq. (3) should have the same displacements] is not the same. The differences in local environment should lead to small departures from the equalities specified in Eq. (3). The fact that $\frac{1}{4}$-order-type spots do not have an exactly zero structure factor and are observed in RHEED measurements[5] also points to the same conclusion.

The slight differences expected in the displacements of nearly equivalent up and down atoms should also have some effect on the surface electronic structure. The double structure at 0.4 and 0.45 eV corresponding to valence-band to empty-surface-state transitions observed in surface photovoltage measurements[7] may be indicative of the size of splitting resulting from the slight inequivalence between similar atoms at the surface. Higher-resolution photoemission spectra would be needed to detect the corresponding splitting of the filled dangling-bond surface state. Surface-atom core-shift measurements and reflectivity[15] and electron-loss[16] measurements similar to those on the 2×1 surface would also be very helpful in providing information on the surface reconstruction.

The different symmetries of the unit cells of the $c$-2×8 and 2×1 surfaces lead to a difference in the maximum number of domains that can occur for each structure. The $c$-2×8 surface, unlike the 2×1 surface, does not have any mirror-reflection symmetry operations through the $xz$ and $yz$ planes, where the $z$ direction is normal to the surface and the $x$ and $y$ directions are along the primitive translation vectors of the rectangular 2×8 unit cell. An equivalent structure, related to the one shown in Fig. 3 by mirror reflection (and having the same LEED spots), is therefore also possible. This suggests that there can be six and not just three domains present on the $c$-2×8 surface.

In conclusion, we find that the reciprocal unit mesh of the $c$-2×8 cell provides a natural explanation for the unusual LEED and RHEED patterns of the Ge(111)8 surface in which many $\frac{1}{8}$-order beams are missing. A structural model for explaining the photoemission data which is based on a buckling of the surface similar to that on the 2×1 surface is also proposed.

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