A period-doubled structure for the 90° partial dislocation in silicon

J. Bennetto, R.W. Nunes, and David Vanderbilt

Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08855-0849

(April 2, 1997)

We suggest that the commonly-accepted core structure of the 90° partial dislocation in Si may not be correct, and propose instead a period-doubled structure. We present LDA, tight-binding, and classical Keating-model calculations, all of which indicate that the period-doubled structure is lower in energy. The new structure displays a broken mirror symmetry in addition to the period doubling, leading to a wide variety of possible soliton-like defects and kinks.

61.72.Lk, 71.15.Fv

Dislocations in silicon and other semiconductors have been well studied both theoretically and experimentally [1]. They are well known to be responsible for plastic behavior, and affect electronic properties as well. The predominant dislocations in silicon lie along the $\langle 110\rangle$ directions, within a $\{111\}$ slip plane, with Burgers vectors at 0° or 60° to the propagation direction. These disassociate into partial dislocations separated by a ribbon of stacking fault. The 0° splits into two 30° partials, while the 60° splits into a 30° and a 90° partial.

The core structure of the 90° partial has received much attention. The unreconstructed core contains a zigzag chain of three-fold coordinated atoms. It has been proposed [2–4] that this dislocation core reconstructs by breaking a $\{110\}$ mirror symmetry, as shown in Figs. 1(a) and 2(a), in order to eliminate the dangling bonds. Thus, each under-coordinated atom forms a new bond with a partner on the other side of the zigzag chain, and the defect core becomes fully saturated. Several workers have shown theoretically [5–12] that this reconstruction lowers the energy by approximately 0.7 eV per unit cell, or 0.18 eV/Å, with respect to the symmetric case. This might be expected, as it restores the four-fold coordination of all the atoms, albeit at the cost of some local bond strain. Moreover, EPR measurements find a low density of dangling bonds, supporting full reconstruction [13]. Thus, a consensus seems to have emerged that this reconstruction represents the physically correct core structure, and a large volume of work has come to rely on this assumption [14–17].

In this Letter, we propose a new structure for the core of the 90° partial dislocation in Si. Our proposed structure retains the four-fold coordination of every atom in the core, but introduces a doubling of the periodicity along the dislocation direction. The new structure is found to be lower in energy than the previously assumed reconstruction, regardless of whether the comparison is based on empirical interatomic potential, total-energy tight-binding, or first-principles density-functional calculations. Thus, it appears likely that all previous work on the 90° partial has assumed an incorrect core structure, and that the interpretation of experimental studies on this dislocation system should be reexamined in light of the new structural model.

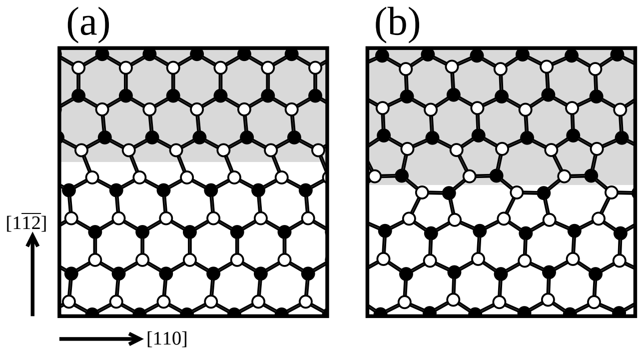

FIG. 1. (a) SP structure of the 90° partial, viewed from above the $(1\bar{1}1)$ slip plane. Shaded region indicates stacking fault. Black (white) atoms lie below (above) the slip plane. (b) Same view of the DP structure.

Our proposed, period-doubled structure is shown in Figs. 1(b) and 2(b). We shall refer to it as the double-period (DP) structure, in contrast to the single-period (SP) structure of Figs. 1(a) and 2(a). The DP structure can be derived from the SP one by inserting alternating kinks at every lattice site along the core. This shifts the center of the dislocation core by one-half lattice spacing along the slip plane, so that the center of the DP core is located halfway between neighboring possible positions of the SP core (Fig. 1). Like the SP structure, the DP one is built entirely out of 5-, 6-, and 7-fold rings. It also retains the symmetry breaking of the SP structure, violating mirror symmetry across the (110) plane. Thus, the DP core has four equivalent ground states, related to each other by (110) mirrors and by single-cell translations. This makes for an especially rich spectrum of solitonic defects and kinks, as we shall see below.

We apply three different approaches to calculate the relative energies of the SP and DP core structures. First, we use the Keating model [18], a classical interatomic potential model containing nearest-neighbor bond stretching and bending force constants. Since both core structures contain only four-fold Si atoms, the Keating energies might be expected to give a reasonable first ap-

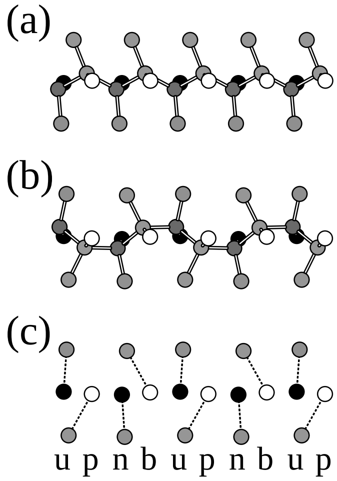

FIG. 2. (a) SP structure (same view as in Fig. 1) but showing only "core" atoms and their neighbors. Darker atoms are farther away. (b) Same view of the DP structure. (c) Schematic representation of (b), in which core atoms have been removed, and second-neighbor connections between remaining atoms are shown. Corresponding symbolic notation is indicated (see text).

proximation. Second, we use a total-energy tight-binding (TETB) approach, in which the electrons are treated quantum-mechanically but in an empirical framework. This approach was implemented using the linear-scaling density-matrix method of Li *et al.* [19], with a real-space density-matrix cutoff of 7.33 Å, and the electron chemical potential in the middle of the band gap. We used the tight-binding parameterization of Kwon *et al.* [20]. Other details are as in Ref. [12]. Third, on system sizes up to about 200 atoms, we carried out *ab-initio* calculations within the local-density approximation (LDA) to density-functional theory. A plane-wave pseudopotential approach was employed, using a Kleinman-Bylander pseudopotential with s-nonlocality only [21], and a plane-wave cutoff of 7 Ry. In all three cases, forces were relaxed to better than 5×10^{-3}eV/Å per atom, with an average force of less than 5×10^{-5}eV/Å.

For calculations on the SP structure, we have constructed supercells containing 96 atoms ("smaller" cell) or 288 atoms ("larger" cell); for the DP structures, these are doubled to 192 and 576 atoms, respectively. In terms of underlying lattice vectors $\mathbf{a}=\frac{a}{2}[1\bar{1}\bar{2}]$, $\mathbf{b}=\frac{a}{2}[110]$, $\mathbf{c}=a[1\bar{1}1]$ representing a 12-atom orthorhombic cell, the 96-atom supercell is defined as $\mathbf{a}'=4\mathbf{a}$, $\mathbf{b}'=\mathbf{b}$, $\mathbf{c}'=2\mathbf{c}+2\mathbf{a}+\frac{1}{6}\mathbf{a}$. The $\mathbf{c}'$ vector is chosen to situate the dislocations in a quadrupole lattice to avoid the spurious shear strains in the minimal dipole cell [8]. (The extra term $\frac{1}{6}\mathbf{a}$ in $\mathbf{c}'$ relieves the strain introduced by the ribbon of stacking fault.) The 192-atom cell has $\mathbf{b}'=2\mathbf{b}$, but is otherwise identical to the 96-atom one. The LDA calculations on these supercells were performed with the

TABLE I. Calculated energy differences between core reconstructions of the 90° partial dislocation, in meV/Å. Cell size refers to the double-period cell. $E_{\rm DP}$ is the energy of the double-period reconstruction. For the single-period case, $\overline{E}_{\rm SP}$ and $\Delta E_{\rm SP}$ are respectively the average and difference of the energies for the two different relative arrangements of mirror symmetry-breaking.

	192-atom supercell		588-atom supercell	
	$E_{\rm DP}-\overline{E}_{\rm SP}$	$\Delta E_{\rm SP}$	$E_{\rm DP}-\overline{E}_{\rm SP}$	$\Delta E_{\rm SP}$
Keating	-22	19	-10	4
TETB	-76	39	-55	8
LDA	-79	47		

two k-points (0,1/8,0), (0,3/8,0) for the DP structure, and the corresponding 4-point set for the SP structure. Empirical and tight-binding calculations were also carried out for enlarged supercells of 288 (SP) or 576 (DP) atoms having lattice vectors $\mathbf{a}'=8\mathbf{a}$, $\mathbf{b}'=\mathbf{b}$ or $2\mathbf{b}$, and $\mathbf{c}'=3\mathbf{c}+4\mathbf{a}+\frac{1}{6}\mathbf{a}$.

Table I shows the results of our total-energy calculations on these cells. For the case of the SP structure, we find that the total energy of the supercell differs noticeably depending on whether the direction of the mirror symmetry-breaking is the same, or opposite, for the two dislocations in the supercell. In the Table, $\overline{E}_{\rm SP}$ refers to the average of these two energies, while $\Delta E_{\rm SP}$ refers to the difference. The corresponding energy splitting is not significant in the DP case. We expect $\overline{E}_{\rm SP}-E_{\rm DP}$ to be a reasonable estimate of the relative energy of SP and DP dislocations in the limit of large supercell size. Note that in all cases $E_{\rm DP}$ is energetically favored not only over $\overline{E}_{\rm SP}$, but also over the preferred of the two SP configurations. In view of the Keating result, it appears likely that the DP structure is preferred because it is able to reduce the local bond strains near the core. Probably this is associated with the fact that the DP structure breaks the (110) mirror symmetry more gently than does the SP one.

Clearly, our results suggest that the DP structure ought to be the physically realized core structure for the 90° partial dislocation in Si. In view of the extensive experimental work on this system, it seems surprising that such a possibility should have been overlooked. However, the two structures do have much in common. Both the SP and DP structures are fully reconstructed, and thus neither gives rise to deep-gap states that would be expected to show an ESR signal. Both are constructed entirely of 5-, 6-, and 7-fold rings, and the maximally strained bonds show comparable distortions in the two cases. Thus, there does not appear to be any obvious signature in electrical or optical properties that would distinguish the DP from the SP structure. Regarding imaging, remarkable progress has been made with transmission electron microscopy (TEM), to the point where individual kinks in the 30° and 90° partials can be re-

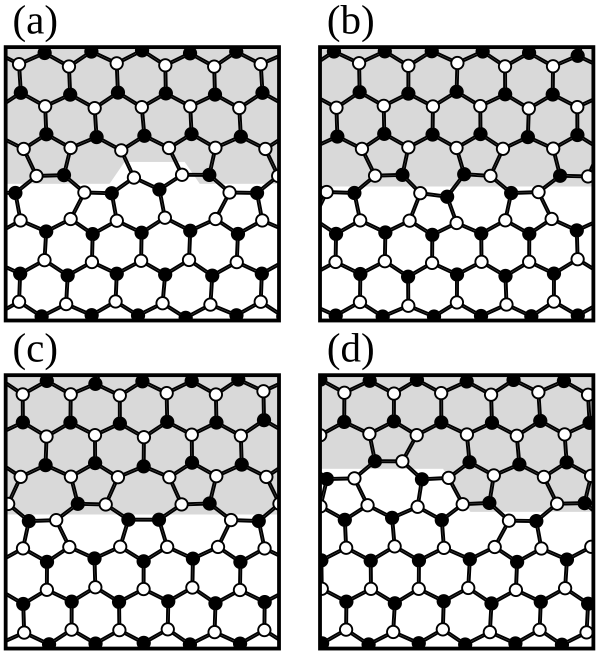

FIG. 3. Examples of several types of core defects in the DP structure. Viewpoint is the same as for Fig. 1. (a) Phase-switching defect (PSD). (b)-(c) Direction-switching defects (DSD). (d) Kink.

solved [22]. While the proposed period doubling is not evident in the 90° core in these images, neither is it visible in the core of the 30° partial, for which a DP structure is well accepted. Nor does it appear possible to locate the position of the 90° core to a resolution of better than half a lattice spacing, which also might distinguish between the SP and DP structures. Thus, it appears that the resolution of TEM is still not adequate to settle this issue. Previous calculations of the activation energies for kink formation and migration in the SP structure [12] were found to be in reasonable (~20%) agreement with experiment, but this agreement may have been fortuitous.

Thus, to our knowledge, present experiments neither rule out nor support our identification of the DP structure as the correct ground-state structure for the 90° partial. It is to be hoped that the present results will stimulate further experimental investigations of this issue. For example, perhaps some kind of imaging electron diffraction technique might be capable of observing the proposed period doubling in the dislocation core.

In the remainder of this Letter, we discuss the structural defects that can occur for the DP core structure, including solitonic and kink structures. We first introduce a shorthand notation for describing the possible core structures and their solitonic excitations. Consider again the DP core structure of Fig. 2(b), showing the central row of core atoms as well as all of their first neighbors. Fig. 2(c) simplifies the picture above it, replacing the central core atoms with dotted lines indicating second-neighbor connections of the remaining off-core neighbors. These are then replaced by a series of lower-case letters that indicate the sequence of directions of these dashed lines (as viewed in two dimensions, from the viewpoint of the black and white atoms): 'u' and 'n' indicate 'up' and 'down', while 'd', 'q', 'p', and 'b' indicate 'upper-right', 'lower-right', 'lower-left', and 'upper-left', respectively (mnemonically referring to the position of the typographic stem of the letter). Thus, the structure of Fig. 1(b) or 2(b) becomes "...upnbupnb..." while that of Fig. 1(a) or 2(a) would be "...nbnb..."

As mentioned earlier, the DP structure breaks two symmetries (mirror and single-period translational symmetries), and has four equivalent ground states ("dnqu", "qudn", "pnbu", "bupn") related to each other by (110) mirrors and by single-cell translations. We first consider the antiphase defect that occurs at a translational domain boundary between core segments; we shall refer to this as a "phase-switching defect" (PSD). The PSD corresponds to a sequence of the form "...bupnbnbu..." [Fig. 3(a)] or "...bupupnbu..." (or their mirror images). As can be seen in Fig. 3(a), a PSD can be regarded as a short segment of the SP structure inserted into the DP one. It is free of dangling bonds, and thus is expected to be a low-energy structural excitation. Due to the presence of the stacking fault, the sequences "...bupnbnbu..." and "...bupupnbu..." are not related by any exact symmetry, and so will have slightly different energies.

A second class of defects results from a reversal of the mirror symmetry-breaking. We shall refer to these as "direction-switching defects" (DSDs); they can be classified by the direction of switching, among other factors. Two examples, "...bup(nu)dnq..." and "...qudnnbup...", are shown in Fig. 3(b) and (c), respectively. [The notation '(nu)' indicates a pair of core atoms bonded to the same out-of-plane atom.] It turns out to be impossible to build a DSD without introducing a dangling bond or an overcoordinated atom, so the DSDs are expected to be more costly than the PSDs. (The malcoordinated atoms do not appear in Fig. 3 as they are located just above or below the plane of the figure.) Combinations of a DSD and a PSD may also occur; these also contain a coordination defect.

We have calculated the energies of several of these defects using the linear-scaling total-energy tight-binding approach. Supercells containing up to 768 atoms were employed. The results are shown in Table II. It can be seen that the DSDs do have a higher energy than the PSDs, as anticipated. Clearly much work remains to be done. One interesting question is that of the interactions between PSDs and DSDs, and whether the formation of a PSD-DSD complex would be exothermic. We also have not yet studied the mobility barriers for these defects.

Finally, we turn to a discussion of kink structures, whose mobility ultimately determines the mobility of the dislocation as a whole. Because there are four degener-

TABLE II. Energies of various defects, given in eV. The notation, described in the text, specifies the entire cell. Energies for the DSDs are given for a matched pair of defects.

PSD	bupnbnbupn	0.42
PSD	bupupnbupn	0.35
DSD+DSD	bup(nu)dnqudnnbupn	1.30
DSD+DSD	bu(pq)udnqudpnbupn	1.37

ate core structures to choose between on each side of the kink, there should be at least 16 distinct kinks. However, each of these is paired with another into which it can be converted by displacing the center of the kink by one lattice constant along the dislocation. (Using a "/" to denote the kink, one such pair would be "...qudnq/bupn..." $\longleftrightarrow$ "...quq/bnbupn...".) Thus, we may distinguish 8 topologically distinct families of kinks. Furthermore, most of these families may be classified as "kink-defect complexes" incorporating either a DSD, or PSD, or both, which may or may not be energetically bound to the kink. Those including a DSD will retain a malcoordinated atom, and will have no reversal of the mirror symmetry-breaking across the kink; those not including a DSD will be fully reconstructed and will show a reversal of the mirror symmetry-breaking. An example of the latter kind is the kink "...udnq/bupn.." shown in Fig. 3(d). Presumably the free energies of formation and migration of such kinks are the key quantities determining the mobility of the 90° dislocation in Si.

In summary, we have proposed a new period-doubled structure for the the 90° partial dislocation in silicon. The new DP structure is predicted to be lower in energy than the SP structure that has been commonly accepted until now. Thus, we suggest that it may be appropriate to reconsider the interpretation of previous experimental work in view of the proposed DP structure. As regards the theoretical work, it is clearly now a high priority to investigate in detail the structure and energetics of defect and kink structures associated with the new core reconstruction.

This work was supported by NSF Grants DMR-91-15342 and DMR-96-13648. One of us (J.B.) wishes to thank N. Marzari for assistance with the LDA calculations.

[1] J. P. Hirth and J. Loathe, *Theory of Dislocations*, (Wiley, New York, 1962).
[2] P. B. Hirsch, J. Phys. (Paris), Colloq., **40**, C6-27 (1979).
[3] R. Jones, J. Phys. (Paris), Colloq. **40**, C6-33 (1979).
[4] S. Marklund, Phys. Status Solidi B **92**, 83 (1979).
[5] S. Marklund, J. Phys. (Paris), Colloq. **44**, C4-25 (1983).
[6] J. R. Chelikowsky, J. C. H. Spence, Phys. Rev. B **30**, 694 (1984).
[7] K. W. Lodge *et al.*, Philos. Mag. A **60**, 643 (1989).
[8] J. R. K. Bigger *et al.*, Phys. Rev. Lett. **69**, 2224 (1992).
[9] S. Marklund and Y.-L. Wang, Phys. Status Solidi B **82**, 137 (1992)
[10] R. Jones et al, Phys. Status Solidi **138**, 369 (1993).
[11] S. Marklund and Y.-L. Wang, Solid State Commun. **91**, 301 (1994)
[12] R. W. Nunes, J. Bennetto, and D. Vanderbilt, Phys. Rev. Lett. **77**, 15417 (1996).
[13] P. B. Hirsch, Mater. Sci. Tech. **1**, 666 (1985).
[14] R. Jones, Philos. Mag. B **42**, 213 (1980).
[15] Philos. Mag. B **48**, 365 (1983).
[16] M. I. Heggie, R. Jones, and A. Umerski, Phys. Stat. Sol **138**, 383 (1993).
[17] L. B. Hansen *et al.*, Phys. Rev. Lett. **75**, 4444 (1995).
[18] Phys. Rev. **145**, 637 (1966).
[19] X.-P. Li, R. W. Nunes, and D. Vanderbilt, Phys. Rev. B **47**, 10891 (1993).
[20] I. Kwon *et al.*, Phys. Rev. B **49**, 7242 (1994).
[21] R. Pérez, M. C. Payne, and A. D. Simpson, Phys. Rev. Lett. **75**, 4748 (1995).
[22] H. R. Kolar, J. C. H. Spence, and H. Alexander, Phys. Rev. Lett. **77**, 4031 (1996).
[23] L. B. Hansen, K. Stokbro, B. I. Lundvist, K. W. Jacobsen (1995).