PHYSICAL REVIEW B VOLUME 56, NUMBER 20 15 NOVEMBER 1997-II

Interaction of vacancies with partial dislocations in silicon

Niklas Lehto
Department of Physics, Luleå University of Technology, S-971 87 Luleå, Sweden

Sven Öberg
Department of Mathematics, Luleå University of Technology, S-971 87 Luleå, Sweden

(Received 24 June 1997)

The interaction of vacancies with 30° and 90° partial dislocations in silicon is examined. In particular, the structures and binding energies are calculated using hydrogen-terminated clusters and local density-functional theory. Moreover the electronic structure is determined using supercells containing dislocation dipoles. Vacancies are found to have binding energies of approximately 2.0 eV and 0.9 eV to 90° and 30° partials, respectively. The elastic strain field of the partials makes the fourfold vacancy reconstruct, which essentially clears the fundamental gap. [S0163-1829(97)52344-7]

Ever since the early days of semiconductor physics, an impressive number of careful investigations have been devoted to the question of which defect levels in the energy gap are due to dislocations. At present, the interaction between point defects and dislocations draws marked attention. One puzzle concerns the question of which type of defects are responsible for the dislocation-related electron paramagnetic resonance (EPR) spectra. This paper will show that there is a large tendency for the dangling bonds of fourfold coordinated vacancies at partial dislocations to reconstruct. This, in turn, essentially clears the fundamental gap, and excludes them from being paramagnetic centers.

Since dislocations interrupt the translational symmetry of the crystal, levels are to be expected in the fundamental gap. In 1953, Shockley[1] proposed that broken bonds in the core of dislocations act as acceptors, and measurements seemed to confirm this idea.[2,3] The present consensus, however, is that this model is not applicable to dislocations in silicon (see, e.g., the review of Hirsch[4]). In particular, perfect 60° and screw dislocations are generally dissociated into 90° and/or 30° partials separated by an intrinsic stacking fault.[5–10] The cores lie between the narrowly spaced {111} planes and can easily be reconstructed with bond lengths differing by only a few percent from bulk.[11–15] The low density of dangling bonds in the core due to reconstruction is confirmed by various experiments.[16–18] These reveal that only a few percent of the core sites of dislocations are occupied by unpaired electrons. Electronic structure calculations show that reconstructed dislocations only give rise to shallow bands.[11–14] Therefore, the experimental data are interpreted in terms of secondary defects. These are, e.g., point defects, reconstruction defects, and kinks, induced along with dislocations during plastic deformation.

Some of these defects, such as kinks, have been excluded. Theoretical work on kinks suggests that they are reconstructed to full coordination and possess only shallow levels.[19,20] This is consistent with electron-beam-induced current experiments.[21] In contrast, there seems little doubt that vacancies bounded to dislocations are electrically active. A recent investigation, using the Keating potential, indicated that vacancies in the core of 90° partials introduce levels in the band gap.[22] In addition, vacancies at 30° partials have been identified to account for the dislocation-related EPR spectra.[23,24] This identification was made by group theoretical analysis of simple defect molecules.

This leads to the scope of this paper, which is to determine the interaction of vacancies with 90° and 30° partial dislocation in silicon. In particular, an *ab initio* local density-functional (LDF) method is used to determine the structures and binding energies of vacancies interacting with these partials. Furthermore, linear combinations of atomic orbitals (LCAO) are used for clarification if they possess deep states in the fundamental gap.

The introduction of dislocations in a lattice changes the topology of the whole system. This, in turn, prevents the characterization of the defect as a local perturbation in a more or less perfect lattice, as is usually possible for point defects. Therefore, a theoretical study of such extended defects is restricted to a finite and relatively small number of unique atoms. There are two approximation methods that could be used. The first is to construct a large finite cluster surrounding the defect and the second is the large unit cell method, which involves forming an infinite superlattice of defects by periodically repeating a large unit cell.

In this paper, the cluster method is applied for the structure optimization, using an *ab initio* LDF method and hydrogen-terminated clusters. This approach is reliable in calculating structures and dynamical properties of semiconductors and their defects.[25,26] It has been successfully used to model dislocations in semiconductors, as well as dislocation-point defect interactions.[15,27,28] Unfortunately, the terminating hydrogen atoms interact strongly with states at the valence- and conduction-band edges, which artificially enlarge the gap. The large unit cell method is, therefore, applied for the electronic structure calculations.

The use of periodic boundary conditions has the advantage of the defect-surface interaction being replaced by a defect-defect interaction at a distance of at least two times larger than for the defect-surface interaction in a cluster. The disadvantage is that it requires the sum of the Burgers vectors in the unit cell to be zero, since otherwise the elastic

 © 1997 The American Physical Society

strain energy of the crystal would be infinite. The unit cell must, therefore, contain at least one dislocation dipole.

The construction of the unit cell starts from an infinite ideal crystal. Cuts are made in zig-zag patterns through it. The cuts parallel to $(1\bar{1}1)$ generate intrinsic stacking faults, and those parallel to $(\bar{1}12)$ generate partial dislocations with alternating Burgers vectors and dislocation lines in the [110] direction. Linear elasticity theory is used to find a first approximation to the structure. From the resulting crystal an oblique unit cell, containing a dislocation dipole, is constructed.

For the 90° partial dipole, the resulting unit cell contains 980 atoms and has a 1.9 nm translation vector along the dislocation line. In the case of the 30° partial dipole, the resulting unit cell contains 1176 atoms and has a 2.3 nm translation vector along the dislocation line. The stacking fault ribbon is 2.3 nm wide and the closest distance between neighboring partials is 2.2 nm. Vacancies are introduced on various sites in these cells, and the structure is calculated by an anharmonic version of Weber's bond charge (ABC) model.[29,30] This results in reconstructed partials and dangling bonds at the vacancy. The dangling bonds at the vacancy are treated with the virtual neighbor approximation.[31]

Clusters of up to 179 silicon atoms surrounding the vacancy are cut from the relaxed cells. The dangling bonds are saturated with hydrogen atoms. These clusters, containing up to 373 atoms, are used in the structure optimization with the *ab initio* LDF method. The method with many applications is reviewed in Ref. 32. Here the electronic wave functions are expanded in s- and p-type Gaussian orbitals centered at nuclei, as well as at bond centers. Norm-conserving pseudopotentials are used in order to exclude core electrons.

The electronic structure is calculated using an LCAO method and periodic boundary conditions, in the manner described above. The crystal potential is a sum of atomic potentials, represented by spherical Gaussians. A set of Gaussian orbitals of s-, p-, and d-type, localized on the atoms of the crystal, is used to expand the Bloch functions of the crystal. Interactions up to fourth-nearest neighbors are included in the calculations, since this accurately reproduces the band structure of silicon.[33]

The basis functions are nonorthogonal, which means that the problem of determining the electronic structure of the crystal is turned into the problem of solving a generalized eigenvalue problem. Since the dimension of the eigenvalue problem is roughly 10 000, the electronic structure is evaluated by the recursion method for nonorthogonal basis functions,[33,34] where the generalized eigenvalue problem is transformed into an eigenvalue problem of a truncated tridiagonal Jacobi matrix. The electronic energy levels are determined from the eigenvalue spectrum of this Jacobi matrix and the local density of states is calculated in the manner described by, e.g., Wang and Lindefelt.[33]

The reconstructed 90° partial in silicon is a stable structure, giving rise to an empty gap, as mentioned above. When a vacancy is introduced, the ABC model shows that the atoms neighboring the vacancy move slightly towards it, but the changes in bond lengths and angles are minute. Yet the introduction of a vacancy releases some of the elastic strain of the partial, which, in turn, binds the vacancy to the core.

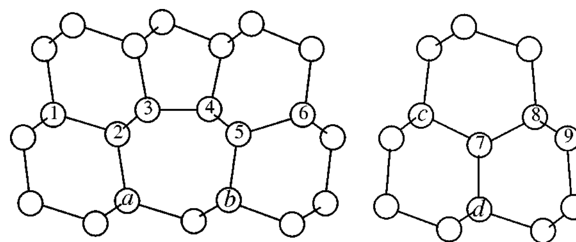

FIG. 1. Reconstructed partials in silicon projected on the (110)-plane. The 90° partial is shown to the left and the 30° partial is shown to the right. The stacking fault is on the right side of both partials. The labeled sites are those referred to in the text.

The most favorable site is found to be the one on the stacking fault side of the core, i.e., site 4 in Fig. 1, which has a vacancy formation energy about 0.6 eV lower than a vacancy formed in a perfect lattice. As shown in Table I, this model predicts a stronger binding to the core than the Tersoff potential used by Marklund.[35]

However, the quantum mechanical interactions between the dangling bonds are not taken into account by the ABC model. Since this is the case, there is a need for a more sophisticated treatment, in order to obtain the correct vacancy structure. This is based on the fact that it cannot predict any Jahn-Teller distortion for a vacancy in an ideal lattice, since this is of a quantum mechanical nature in contrast to the interactions in the ABC model, which are of a pure elastic nature.

When the vacancy is located in the vicinity of a partial dislocation, the strain field and, at some sites, the local geometry opens up the possibility of a pairwise reconstruction of the dangling bonds. This is shown in Fig. 2 for a vacancy in the core of a 90° partial. Calculations using the *ab initio* LDF method confirm that this reconstruction really occurs at most sites close to partials. This reconstruction is significantly stronger than the Jahn-Teller distortion of the ideal vacancy. It is forced by the fact that the tetrahedral symmetry of the vacancy is *a priori* broken by the elastic strain field of the dislocation.

For a vacancy at a core site of a 90° partial, i.e., at site 3 or 4, the two reconstructed bonds are only stretched by about

TABLE I. The difference in formation energy, ΔU_f, on various sites in the vicinity of the normally reconstructed 90° partial dislocation in silicon. The formation energies are calculated using the local density-functional method (LDF), the anharmonic bond charge model (ABC), and the Tersoff potential. Zero formation energy is at the site giving the lowest energy for each method. The sites are numbered according to Fig. 1.

		ΔU_f (eV)	
Vacancy position	LDF	ABC	Tersoff[a]
1	+1.889	+0.502	+0.344
2	+1.342	+0.344	+0.082
3	+0.125	+0.012	0.0
4	0.0	0.0	+0.008
5	+1.388	+0.347	+0.098
6	+2.012	+0.502	+0.364
Ideal		+0.596	+0.382

[a]See Ref. 35.

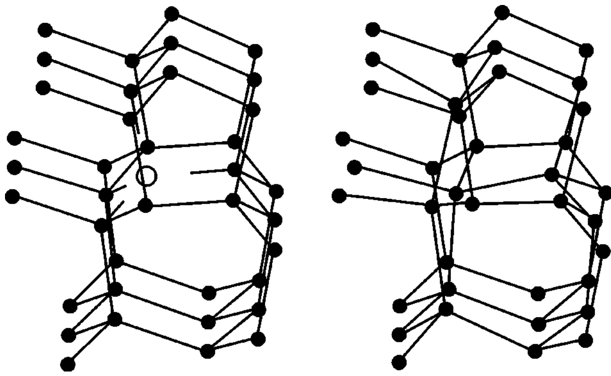

FIG. 2. When a vacancy is located at a core site of the normally reconstructed 90° partial dislocation in silicon, as indicated by the circle in the left figure, the neighboring atoms are able to relax so that reconstructed bonds are formed, as shown to the right.

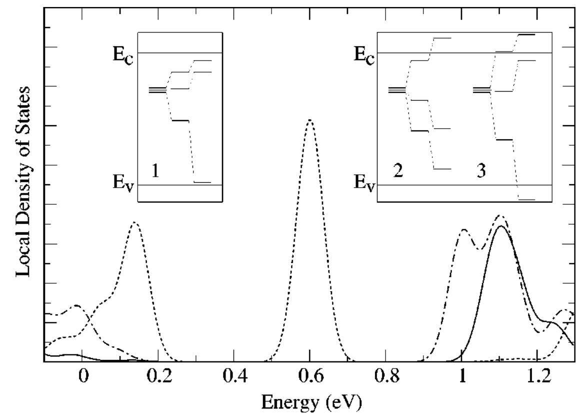

FIG. 3. The density of states projected on s-p hybrids on atoms neighboring vacancies at site 1 (dashed-dotted line), 2 (dotted line), and 3 (solid line). The valence-band edge (E_v) is at *zero*, and the conduction-band edge (E_c) is at 1.17 eV. The insets show the energy-level splitting, first by the elastic strain field of the 90° partial, and then by the additional reconstruction of the dangling bonds.

9 and 15 % compared with the ideal. In addition, one of the back bonds is stretched by 12%. When the vacancy is moved to site 2 or 5 only one bond is fully reconstructed with a bond stretch of 13%, whereas the other bond is about 50% longer than ideal. Outside the dislocation, at site 1 or 6, the reconstruction is again realized, but here the bonds are stretched by up to 20%. The energetically most favorable vacancy site is found to be site 4, which is the one on the stacking fault side of the core. As shown in Table I, the vacancy formation energy is about 2.0 eV higher on a site outside the partial than on a site in the core.

The dangling bonds of a vacancy at a 30° partial are also found to be reconstructed, but the reconstruction is somewhat weaker than for vacancies at 90° partials. When the vacancy is located in the core of a 30° partial, at site 7, the two bonds are stretched by 19 and 14 %, respectively. At site 8 the bonds are stretched by 10 and 19 %, and outside the core, at site 9, the bonds are 19 and 25 % longer than the ideal. The binding energy of vacancies at sites 7 and 8 only differ by 0.03 eV in favor of the noncore site 8. In comparison, the energy is about 0.9 eV higher on the site outside the 30° partial. This binding energy is lower than the 1.9 eV reported by Teichler.[36]

Electronic structure calculations on the ideal vacancy in silicon show a threefold degenerate state in the fundamental gap, 0.84 eV above the valence-band edge (E_v). The symmetry of this level is T_2 in the representation of the T_d group, and the wave function of this state is mainly of p character. This is in agreement with earlier work.[37]

When the vacancy is moved into the strain field of a 90° partial the threefold degenerate level splits into nondegenerate levels, since the tetrahedral symmetry is broken. The largest splittings arise when the vacancy is located in the core of the partial, i.e., at site 3 or 4, where the levels are found at $E_v+0.40$ eV, $E_v+0.83$ eV, and $E_v+1.18$ eV. This splitting is smaller than the one found by Marklund and Wang, using the Keating potential for the relaxation.[22] Here, as in the work by Marklund and Wang, the splitting is due only to the symmetry breaking induced by the elastic strain field of the partial.

When the quantum mechanical interactions between the dangling bonds are included, using the LDF method, the vacancy reconstructs in the way discussed. The recursion method, as well as the Kohn-Sham cluster levels, show that this reconstruction clears the fundamental gap from electronic states, except for some shallow ones. This result is in contrast to what was found in Ref. 22 and the general belief that vacancies in the core of dislocations are electrically active. In the case of a not fully reconstructed vacancy, as found at sites 2 and 5 of the 90° partial, states are found at midgap. These states are due to dangling bonds at the atoms a and 3, or b and 4. The line connecting these atoms deviate by an angle of about 8° from a local $\langle 011 \rangle$ binding direction. There are four possible orientations of this connection line depending on which side of the partial the vacancy is located and on the reconstruction sense of the partial. Similar to isolated vacancies in silicon, this defect is expected to be paramagnetic only when charged. The local density of states and the level splitting are shown in Fig. 3 for vacancies located at sites 1, 2, and 3 of the 90° partial.

A threefold coordinated vacancy in the core of a 30° partial has also been investigated. This defect, which is a vacancy at site 7 together with a reconstruction defect, has been identified as being responsible for the Si-Y line in the dislocation-related EPR spectra.[24] This identification was made under the assumption that atom 8 is distinguished from the atoms c and d, and that the distance $\overline{cd}$ is larger than the distances $\overline{c8}$ and $\overline{d8}$. The calculations made here show that this threefold coordinated vacancy gives rise to a level at $E_v+0.61$ eV, which is due to dangling bonds at the atoms c and 8. The distance $\overline{c8}$ is 46% longer than ideal bond lengths whereas the bonds $\overline{d8}$ and $\overline{cd}$ are found to be 22% longer than ideal. This should be a paramagnetic center, but the defect orientation is different than that assumed in Ref. 24.

This paper has shown that the binding energy of a vacancy to the core of 90° partial dislocations in silicon is at least 2.0 eV, which is notably higher than the binding energy of 0.9 eV, found for vacancies at 30° partials. Furthermore, it has shown that fourfold coordinated vacancies located in the vicinity of 30° and 90° partial dislocations possess no deep electronic states. Exceptions to this are found at some ener-

getically unfavorable sites close to the core of the 90° partial. These unfavorable sites are neighbors to the core atoms and lie in the seven-atom ring in the elastically expanded region of this partial. The cleared gap is an effect of a reconstruction of the dangling bonds introduced along with the vacancy. Finally, there are different vacancy sites close to the core of a 30° partial with almost the same binding energy. This might explain that high-resolution electron microscopy[38] shows the core of 30° partials to be blurred in contrast to the cores of 90° partials.

We thank the High Performance Computing Center North in Sweden for computer time on the IBM RS/6000 SP system in Umeå.

[1] W. Shockley, Phys. Rev. **91**, 228 (1953).
[2] W. Schröter, Inst. Phys. Conf. Ser. **46**, 114 (1978).
[3] S. Mantovani, U. del Penino, and E. Mazzega, Phys. Status Solidi B **35**, 451 (1976).
[4] P.B. Hirsch, Mater. Sci. Technol. **1**, 666 (1985).
[5] I.L.F. Ray and D.J.H. Cockayne, Proc. R. Soc. London, Ser. A **325**, 543 (1971).
[6] F. Häussermann and H. Schaumburg, Philos. Mag. **27**, 745 (1973).
[7] A. Gomez, D.J.H. Cockayne, P.B. Hirsch, and V. Vitek, Philos. Mag. **31**, 105 (1975).
[8] K. Wessel and H. Alexander, Philos. Mag. **35**, 1523 (1977).
[9] G.R. Anstis *et al.*, Inst. Phys. Conf. Ser. **60**, 15 (1981).
[10] A. Bourret, J. Desseaux, and C. D'Anterroches, Inst. Phys. Conf. Ser. **60**, 9 (1981).
[11] S. Marklund, J. Phys. (Paris) **44**, C4-25 (1983).
[12] R. Jones, J. Phys. (Paris) **40**, C6-33 (1979).
[13] M. Heggie and R. Jones, Inst. Phys. Conf. Ser. **87**, 367 (1987).
[14] K.W. Lodge *et al.*, Philos. Mag. A **60**, 643 (1989).
[15] M. Heggie, R. Jones, and A. Umerski, Philos. Mag. A **63**, 571 (1991).
[16] H. Alexander, in *Dislocations in Solids*, edited by F.R.N. Nabarro (North Holland, Amsterdam, 1986), Vol. 7, p. 113.
[17] P.R. Wilshaw and G.R. Booker, Inst. Phys. Conf. Ser. **76**, 329 (1985).
[18] R. Woodham and G.R. Booker, Inst. Phys. Conf. Ser. **87**, 787 (1989).
[19] R. Jones, Philos. Mag. A **42**, 213 (1980).
[20] M. Heggie and R. Jones, Philos. Mag. B **48**, 365 (1983).
[21] P.R. Wilshaw and T.S. Fell, Inst. Phys. Conf. Ser. **104**, 85 (1989).
[22] S. Marklund and Wang Y.-L., Phys. Status Solidi B **189**, 473 (1995).
[23] C. Kisielowski-Kemmerich, Inst. Phys. Conf. Ser. **104**, 187 (1989).
[24] C. Kisielowski-Kemmerich, Phys. Status Solidi B **161**, 11 (1990).
[25] P. Briddon and R. Jones, J. Phys.: Condens. Matter **1**, 10 361 (1989).
[26] R. Jones and S. Öberg, Phys. Rev. Lett. **68**, 86 (1992).
[27] S. Öberg *et al.*, Phys. Rev. B **51**, 13 138 (1995).
[28] P. Sitch *et al.*, Phys. Rev. B **50**, 17 717 (1994).
[29] J. Wilder, Diploma thesis, University of Göttingen, 1995.
[30] W. Weber, Phys. Rev. B **15**, 4789 (1977).
[31] S. Marklund, Phys. Status Solidi B **100**, 77 (1980).
[32] R. Jones, Philos. Trans. R. Soc. London, Ser. A **350**, 189 (1995).
[33] Wang Y.-L. and U. Lindefelt, Phys. Rev. B **37**, 1320 (1988).
[34] R. Jones and T. King, Philos. Mag. B **47**, 491 (1983).
[35] S. Marklund, Solid State Commun. **72**, 609 (1989).
[36] H. Teichler, in *Polycrystalline Semiconductors II*, edited by J.H. Werner and H.P. Strunk, Springer Proceeding in Physics Vol. 54 (Springer-Verlag, Heidelberg, 1991), p. 134.
[37] U. Lindefelt and Wang Y.-L., Phys. Rev. B **38**, 4107 (1988).
[38] A. Bourret, J. Desseaux-Thibault, and F. Lancon, J. Phys. (Paris) **44**, C4-15 (1983).