PHYSICAL REVIEW B VOLUME 47, NUMBER 19 15 MAY 1993-I

Ab initio investigation of carbon-related defects in silicon

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(Received 15 June 1992; revised manuscript received 28 September 1992)

Ab initio total-energy calculations based on the local-density-functional, pseudopotential, and supercell approximations are performed to investigate carbon defects in silicon. The geometry and the formation energy of substitutional and impurity-vacancy defects are studied including the relaxation of nearest and next-nearest neighbors. Results for substitutional carbon appear to be consistent with a recently suggested reinterpretation of the available experimental formation energy data. Results for the interaction energy between a carbon atom and a silicon vacancy predict a small binding energy of 0.19 eV.

I. INTRODUCTION

Carbon holds a special position among impurities in silicon. It is an isovalent impurity, and it is one of the most common impurities[1] in silicon. Carbon is usually found in concentrations as high as 10^{18} cm^{-3} in Czochralski-grown samples. Due to its frequent presence in such samples, its related centers are technologically important. Another interesting aspect is that some carbon-based defect complexes[2,3] have been reported to exhibit metastability.

It is well established that carbon and other isovalent impurities prefer to dissolve substitutionally in silicon and that these substitutional centers are electrically inactive in the neutral charge state. The most interesting feature is the variety of defect complexes that are carbon based. These defects arise from the ability of carbon atoms to aggregate or interact with native defects or with other impurities such as phosphorus[2] or oxygen.[4] These defect complexes are generally not well understood.

Tersoff,[5] using a parametrized classical potential, has recently performed the most extensive theoretical study of carbon defects in silicon to data. While the ability of classical potentials to describe properties of real materials accurately is somewhat controversial, his results exhibit good agreement with experiment for several defect configurations. A notable exception, however, is the formation energy[6] of substitutional carbon in silicon. This discrepancy has led to questions[5] regarding the original interpretation of the experimental data. In this work, we present an *ab initio* determination of this formation energy that appears to reinforce Tersoff's reinterpretation of the experimental data.

Another related issue is the nature of the interaction between the substitutional carbon and the silicon vacancy. Classical calculations[5] predict that the nearest-neighbor interaction between vacancy and substitutional C (intimate carbon-vacancy pair) is weakly repulsive. Moreover, this result appears to be consistent with the lack of experimental observation of bound carbon-vacancy pairs. In this work, however, we perform *ab initio* calculations on the intimate carbon-vacancy pair that predict that it is in fact very weakly bound. The results of these calculations also provide an explanation of the mechanism responsible for binding and why the carbon-vacancy pairs have not been observed experimentally.

This paper is organized as follows. Section II presents a brief description of the computational procedure. Section III presents the results of lattice relaxation of substitutional carbon and germanium and the formation energy of substitutional carbon. Section IV exhibits the results of lattice relaxation and binding energy for the intimate carbon-vacancy pair. Finally, in Sec. V we present concluding remarks.

II. COMPUTATIONAL PROCEDURE

First-principles computational procedures, such as *ab initio* pseudopotential total-energy methods, have proven themselves as very reliable tools for the study of defects in semiconductors. In this investigation we have applied one such method to study carbon-related defects. Our calculations are based on the density-functional theory[7] and performed within the quantum conjugate gradient approach in the form presented by Teter, Payne, and Allan.[8] The exchange-correlation functional was approximated as a local-density functional with Ceperley-Alder parametrization[9] of the Perdew-Zunger[10] form. We have employed separable norm-conserving nonlocal pseudopotentials generated as described by Rappe *et al.*[11] and 32-atom bcc supercells to deal with the defects in the context of Bloch's theorem. The cutoff energy for the plane-wave basis set was 40 Ry in the case of the carbon defects and 12 Ry for the auxiliary calculations involving germanium defects. For *each* calculation the *k*-point summations were performed using the γ point and the Baldereschi[12] *k*-point. As the carbon-vacancy pair presents lower symmetry than other defects studied here, we decided not to impose any symmetry *a priori*. This leads to a consistent procedure to study all defects but increases the computational effort considerably. Under these conditions, the Baldereschi point corresponds to 24 k points in the full Brillouin zone.[12] The formation energies calculated using the γ point or Baldereschi point differ by less than 0.02 eV, indicating that k-point convergence is obtained. Previously, the same procedure was extensively tested on oxygen defects in silicon[13,14] and it proved to yield reliable results. Relaxed configurations were obtained by minimizing the total energy with respect to the atomic positions of nearest and next-nearest neighbor of the defects. Long-range relaxation was obtained by coupling local-density approximation (LDA) calculations with a conventional valence force field.[15] In order to calculate the relaxation and the formation energy of the defects, many total-energy calculations were performed. Thus the described approach was applied to the following systems: substitutional C in silicon (Si:C_S), intimate carbon-vacancy pair in Si (Si:CV), substitutional Ge in Si (Si:Ge_S), and germanium-vacancy pair in Si (Si:GeV). auxiliary calculations for pure crystalline silicon (c-Si), silicon vacancy (Si:V), and silicon carbide (SiC) were also performed.

III. FORMATION ENERGY OF SUBSTITUTIONAL CARBON

We have studied the relaxation induced in the silicon lattice by the substitutional isovalent impurities (C,Ge) in silicon. These results are presented in Table I. Our calculations show that the relaxation of the lattice in response to a carbon impurity is very different from the relaxation about a germanium impurity. The presence of a substitutional carbon atom induces strong relaxation of the neighboring silicons. The silicons that are nearest neighbors to the carbon undergo a large movement towards the impurity so that C-Si bond length is smaller than that of a normal Si-Si bond by 0.35 Å (~15%). Its next-nearest neighbors are affected as well, but their displacement towards the carbon atom is much smaller. In the case of substitutional germanium, the lattice relaxation is much weaker. The bond distance between Ge and its silicon neighbors is only ~2% longer than a normal Si-Si bond and the next-nearest neighbors practically do not move from their normal lattice positions. The strong relaxation induced on the lattice by the carbon atom explains our choice of a large supercell to study carbon defects in silicon. The geometry optimization is a necessary intermediate result to calculate the formation energy of the defect.

TABLE I. Lattice relaxation induced by substitutional isovalent impurities in silicon. Here d_1 represents the distance from the substitutional site to its nearest neighbors and d_2 represents the distance to next-nearest neighbors. For comparison, the central column shows these distances for pure crystalline silicon.

	Impurity		
	C	Si	Ge
d_1 (Å)	2.00	2.35	2.38
d_2 (Å)	3.76	3.84	3.84

TABLE II. Formation energy (in eV) of carbon defects in silicon. The first row presents the results of substitutional carbon in silicon, the second row corresponds to the neutral vacancy, and the third row to the carbon-vacancy pair. The LDA column presents the results of this work, the Classical column presents the results of Ref. 5, and the Experimental column shows the results of measurements performed in Refs. 6 and 17 for Si:C_S and Si:V, respectively.

	Formation energy		
Defect	LDA	Classical	Experimental
Si:C_S	1.89	1.6	2.3±0.3
Si:V	3.75	3.7	3.6±0.2
Si:CV	5.45	5.5	

The formation energy of substitutional carbon in silicon was then obtained from our *ab initio* calculations. The determination of the formation energy of a defect involves the choice of a reservoir of the impurity. In our case, silicon carbide is used as the source of C atoms that are introduced in silicon. This procedure is formally equivalent to the one used in Ref. 5 so that our results can be directly compared to those. For this reason, an *ab initio* total-energy calculation of pure silicon carbide was performed. Our results for pure silicon carbide were in excellent agreement[16] with experimental and previous theoretical calculations.

Table II presents the formation energy of substitutional carbon in silicon as obtained in this work and compares it to other theoretical and experimental results. Notice that our *ab initio* result is closer to the one obtained from a classical calculation than to the original interpretation of the experiment. The experimental value was determined by a fit to the solubility data, which yielded a concentration of $3.5\times10^{24}\exp(-2.3/kT)$ cm^{-3}. However, Tersoff[5] pointed out that there is no particular reason for treating the prefactor for the solubility experiment as a free parameter. The equilibrium concentration is expected to be $5\times10^{22}\exp(-D/kT)$ cm^{-3}. Here, 5×10^{22} cm^{-3} is simply the atomic density of pure silicon, and D is the energy of substitution per atom. Combining the theoretical prefactor with our *ab initio* formation energy (1.89 eV), an excellent agreement with the experimental data can be obtained for the entire range of temperatures of the experiment. Furthermore, at high temperatures where the measurement should be most reliable the theoretical curve improves the agreement with the data. Therefore we support the reinterpretation of the experimental data suggested by Tersoff.

IV. CARBON-VACANCY PAIR IN SILICON

Next, we studied the relaxation produced by defect complexes consisting of an intimate pair-substitutional isovalent impurity (C or Ge) and a vacancy. In this case, again, the relaxations induced by C and Ge are dramatically different. Germanium tends to move towards the vacancy, making longer bonds with its nearest neighbors.

Carbon moves away from the vacancy and becomes threefold coordinated. It is also worth noticing that the carbon atom and its three silicon neighbors are almost coplanar. In this case, the Si-C bonds are much more graphitelike than diamondlike. These features are presented in Fig. 1 along with perfect silicon for comparison.

The binding energy of a defect complex can be obtained as the energy difference between the total formation energy of the isolated defects and the formation energy of the defect complex. Thus the formation energies of the isolated vacancy (Si:V), the substitutional carbon (Si:C_S), and the pair are necessary to determine the binding energy of a carbon-vacancy pair. Table II presents these values and compares them to the classical potential calculation. Notice that the *ab initio* calculation, in contrast to the classical one, predicts that the Si:CV binds. The calculated binding energy is very small, 0.19 eV. In this case, we believe that the classical potential is not able to describe accurately the tendency of the carbon atom to rehybridize. Due to the small binding energy calculated, which is of the same order of magnitude of the usual accuracy associated with the local-density approximation, our result must be considered as an indication of binding rather than a definitive proof.

If indeed Si:CV can form bound pairs, why is it that they appear not to have been observed experimentally? We believe that this is related to the electronic inactivity of this defect. To understand the electronic structure of this defect complex, it is useful to make a comparison with the neutral silicon vacancy. The unrelaxed (tetrahedral, T_d) vacancy has a nondegenerate a_1 level in the valence band and a triply degenerate t_2 level in the gap. However, since this degenerate level is partially filled, Jahn-Teller distortion lowers the system energy and the relaxed defect has a nondegenerate filled level in the gap as well as a doubly degenerate unfilled level in the gap. The unrelaxed and the relaxed carbon-vacancy pair both have the same C_{3v} symmetry. The symmetry lowering is due to the presence of the impurity adjacent to the vacancy, not the Jahn-Teller effect. The resulting defect levels are qualitatively similar to those of the neutral vacancy, with two nondegenerate filled states. However, due to the high electronegativity of carbon, the highest filled state of Si:CV is much lower in energy than the corresponding one of the neutral vacancy. Thus it becomes important to determine the position of this level relative to the top of the valence band. Due to the supercell nature of our calculations, a weak interaction between cells is always present and this level is transformed into a fairly flat band. To determine the exact position of the level, we fit the energy values for this band with a simple tight-binding (TB) model. This model allows us to remove the interaction among cells in a straightforward way and yields the real position of the level. Firstly, the charge density was analyzed to understand the characteristics of the band. The charge distribution of this highest filled band strongly resembles that of a p orbital centered on the carbon atom pointing along the (111) direction (towards the vacancy). Therefore our TB model is simply a bcc crystal with one atom and one p orbital per unit cell. After a fit based on the least-squares method, the level position was determined to be 0.34 eV below the top of the valence band. From this analysis, it is possible to understand why this defect would be difficult to observe. In neutral or p-type silicon, this defect is not electrically active and the usual experimental techniques would not recognize it. Possibly, infrared measurements, vacancy mobility experiments, or electrical measurements in n-type silicon could lead to an observation of this defect.

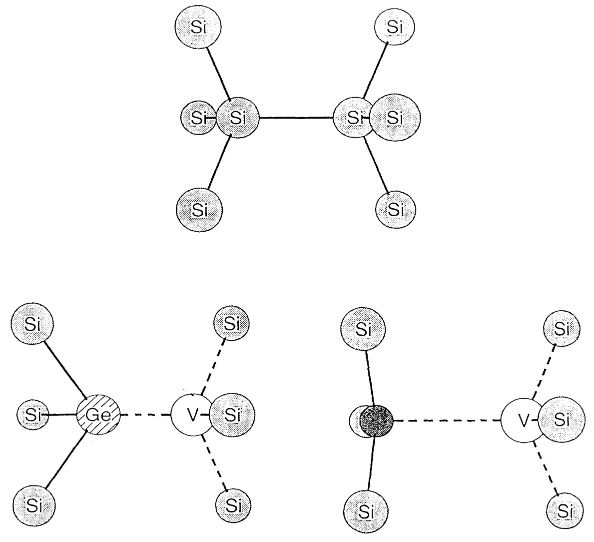

FIG. 1. Schematic representation of intimate substitutional-vacancy pairs in silicon. The atoms are indicated by shaded circles with their chemical symbols, except for carbon, which is represented by a solid gray circle. The silicon vacancies are indicated by V and represented by open circles, and the bonds broken due to the presence of the vacancy are shown as dashed lines. Top: silicon fragment in the absence of defect (for comparison). Bottom left: germanium-vacancy pair in silicon. Bottom right: carbon-vacancy pair in silicon.

V. FINAL REMARKS

We have used an *ab initio* total-energy approach to determine the formation energy of substitutional carbon in silicon. Our result agrees with a previous classical potential calculation and provides further evidence in support of the reinterpretation of the original experimental data. The relaxation of the next-nearest neighbors of this defect and its importance to the formation energy are explained.

It is calculated that an intimate carbon-vacancy pair in silicon will bind with a weak binding energy of ~ 0.2 eV. Due to the smallness of this value, we present this result as an intriguing possibility. Indeed, it is also intriguing that the electronic states associated with this bound defect reveal an electrical inactivity that is consistent with its lack of observation to date.

ACKNOWLEDGMENTS

The authors want to thank Professor G. D. Watkins for helpful discussions and Dr. T. A. Arias for his help with the computer programs. A.D.P., Jr. is grateful to Conselho Nacional de Pesquisa e Desenvolvimento Tecnologico (CNPq, Brazil). A.M.R. thanks the Joint Services Electronics Program. This work was partially supported by grants from the Office of Naval Research Center through ONR Contract Nos. N00014-86-K-0158 and N00014-84-C-0396. We also thank the staff of the San Diego Supercomputer facility, where most of the calculations were performed.

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[1] For an overview, see *Oxygen, Carbon, Hydrogen and Nitrogen in Crystalline Silicon,* edited by J. L. Mikkelsen, Jr. *et al.*, MRS Symposia Proceedings No. 59 (Materials Research Society, Pittsburgh, 1986).

[2] X. D. Zhan and G. D. Watkins, Appl. Phys. Lett. **58**, 2144 (1991).

[3] L. W. Song, X. D. Zhan, B. W. Benson, and G. D. Watkins, Phys. Rev. Lett. **60**, 460 (1988).

[4] H. Katayama-Yoshida and T. Sasaki, in *20th International Conference on the Physics of Semiconductors,* edited by E. M. Anastassakis and J. D. Joannopoulos (World Scientific, Singapore, 1990), Vol. 1, p. 561.

[5] J. Tersoff, Phys. Rev. Lett. **64**, 1757 (1990).

[6] A. R. Bean and R. C. Newman, J. Phys. Chem. Solids **32**, 1211 (1971).

[7] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

[8] M. Teter, M. Payne, and D. Allan, Phys. Rev. B **40**, 12 255 (1989).

[9] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[10] J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1984).

[11] A. M. Rappe, K. M. Rabe, E. Kaxiras, and J. D. Joannopoulos, Phys. Rev. B **41**, 1227 (1990).

[12] A. Baldereschi, Phys. Rev. B **7**, 5212 (1973).

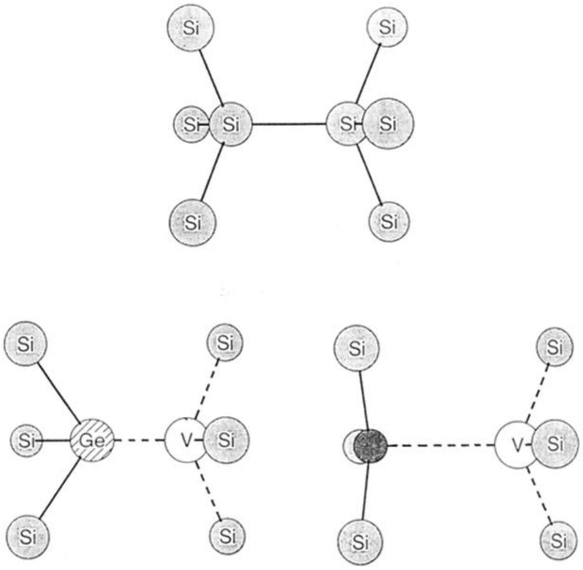
[13] M. Needels, J. D. Joannopoulos, Y. Bar-Yam, S. T. Pantelides, and R. H. Wolfe, in *Defects in Materials,* edited by P. D. Bristowe, J. E. Epperson, J. E. Griffith, and Z. Liliental-Weber, MRS Symposia Proceedings No. 209 (Materials Research Society, Pittsburgh, 1991), p. 103.

[14] A. Dal Pino, Jr., M. Needels, and J. D. Joannopoulos, Phys. Rev. B **45**, 3304 (1992).

[15] P. N. Keating, Phys. Rev. **145**, 637 (1966).

[16] The computed lattice constant of *c*-SiC in the diamond structure at $T = 0$ K differs from the experimental one by less than 1%.

[17] S. Dannefaer, P. Mascher, and D. Kerr, Phys. Rev. Lett. **56**, 2195 (1986).



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