Carbon Defects and Defect Reactions in Silicon

J. Tersoff
IBM Research Division, T. J. Watson Research Center, Yorktown Heights, New York 10598
(Received 3 January 1990)

The energies of carbon defects in silicon are calculated, using an empirical classical potential, and used to infer defect properties and reactions. Substitutional carbon is found to react with silicon interstitials, with the carbon "kicked out" to form a (100) split interstitial. This interstitial can in turn bind to a second substitutional carbon, relieving stress, in three configurations with similar energies. The results here accord well with a variety of experimental data, including defect structures, activation energies for defect motion, and coupling to strain. A discrepancy with the accepted values for carbon solubility in silicon suggests a reinterpretation of the experimental data.

PACS numbers: 61.70.Rj, 61.70.Bv, 61.70.Yq, 71.45.Nt

In recent years there has been tremendous progress in the theoretical understanding of both dopant and native defects in silicon.[1] However, no comparable study has been made of isovalent impurities. Yet carbon is a ubiquitous and important impurity in silicon, exhibiting a wealth of interesting configurations.[2]

As a first step towards a fuller theoretical understanding, extensive calculations of carbon defects in silicon have been performed, using an empirical classical potential[3] to model the atomic interactions. Specific issues addressed here include the solubility of C in Si, its diffusion, the formation, migration, and structural properties of interstitial C, and the binding of C interstitials to substitutional C, to form C complexes. The results, summarized in Tables I and II, are in accord with experimental data for a striking variety of properties, confirming the value of the present simple approach for initial studies of this challenging system.

TABLE I. Formation energy (in eV) of defects in silicon containing one carbon atom, and of their two-C complexes with a substitutional carbon. The silicon vacancy is also included, to show its interaction with substitutional C. Labels of two-C complexes are explained in text.

Defect	Energy of defect	Energy of complex	Label of complex
Substitutional	1.6		
Si vacancy	3.7	5.0	
Interstitials[a]			
B	5.3	5.1	CSC
		6.4	CCS
S	4.6	5.1	SCSC
		5.2	SCCS
		6.3	SSCC
X	5.9		
T	[3.8[b]]	7.4	
H	6.7		

[a] Labels *B*, *S*, *X*, *T*, and *H* denote bond centered, (100) split, exchange [i.e., (110) split], tetrahedral hollow site, and hexagonal hollow site; see Ref. 1 for structures.

[b] This small value is believed to be an artifact of the short cutoff distance used; see Ref. 13 for discussion.

As expected, the lowest-energy form of C in Si is found to be substitutional C. The calculated activation energy for substitutional diffusion is a bit less than 4 eV, in reasonably good agreement with experiment.[4] Comparison of substitutional and interstitial energies indicates that a Si self-interstitial can "kick out" substitutional C, or form a C interstitial in the (100) split configuration, precisely the process which has been observed.[5] The interstitial's migration energy, and its elastic coupling tensor, are in good agreement with experiment.[5]

The interstitial can in turn bind with another substitutional C; the compressive stress of the interstitial C tends to cancel the tensile stress of the substitutional C. The predicted structures for this complex accord with those observed by Song *et al.*[6]

TABLE II. Calculated activation energies, and strain coupling constants, for C defects in Si (in eV); and experimental values for comparison.

Property	Calculation	Experiment
Energy of substitution	1.6	1.5,[a] 2.5,[b] 1.7[c]
Interstitial migration	≥0.7[d]	0.9[e]
Diffusion	3.9	3.1[f]
Interstitial C A_{ij}		
A_{11}	8	7[e]
A_{22}	−1	0
A_{33}	−7	−7

[a] Reference 8.

[b] Reference 7.

[c] From reevaluation of Ref. 7; see text and Ref. 12.

[d] 0.9 eV if include estimated barrier of 0.2 eV between *S* and *B* interstitials; see text.

[e] Reference 5.

[f] Reference 4.

The enthalpy of solution for substitutional C has been measured[7,8] as 2.3 eV. Here the energy is calculated as 1.6 eV, an apparent discrepancy. However, simple considerations discussed below suggest that the experiment can be more consistently interpreted as giving an energy of 1.7 eV, in good agreement with the present calculation.

The empirical classical potential used here to calculate the energies has been presented elsewhere.[3] It begins with potentials derived earlier for elemental Si and C; parameters describing Si-C interactions are determined from the elemental parameters by an interpolation scheme. This approach is necessarily less accurate than "first-principles" methods, and neglects electronic degrees of freedom. However, by simplifying the calculations, it permits us to get a broad view of the possible defects and reactions, tying together a large body of experimental data.

Extensive tests have confirmed the suitability of this method for treating point defects, including isovalent impurities.[3] In particular, results for C and SiC have been compared[3] with "state-of-the-art" quantum-mechanical calculations of Bernholc and co-workers.[9,10] The present method is rather successful in treating point defects in those materials, including antisite defects. There is thus ample reason to expect comparable accuracy for C in Si.

The potential here differs from that described earlier[3] only in a small change of the parameters for carbon. The parameters[11] used here are constrained to reproduce the energy of the vacancy in diamond, as calculated by Bernholc *et al.*,[9] at the expense of a poorer description of graphite, which was deemed less relevant for the present application. (In the defects studied here, three-coordinated C atoms have no opportunity for π bonding. This is similar to the vacancy in diamond, but in contrast to graphite.) In addition, since we are not concerned with dynamical simulations, where the potential must go smoothly to zero with distance, the potential is here abruptly truncated at 2.5 Å, consistent with the original nearest-neighbor-only picture.[11] This short cutoff leads to problems only in the case of the tetrahedral interstitial, discussed below.

For consistency, we refer in Table I and throughout to the free energy of formation, $E-N_{\text{Si}}\mu_{\text{Si}}-N_{\text{C}}\mu_{\text{C}}$. The chemical potentials μ_{Si} and μ_{C} are -4.63 and -7.70 eV here, determined by equilibrium with Si (cohesive energy 4.63 eV/atom with the present potential), and with SiC (12.33 eV per formula unit). All structures are fully relaxed in a cubic cell 16.3 Å on a side (216 atoms without defects), with periodic boundary conditions, at zero temperature.

The natural place to begin is with substitutional C, since this is the simplest and most common carbon defect in Si. From elementary statistical mechanics,[12] the equilibrium concentration is expected to be $5\times10^{22}\exp(-\Delta/kT)$ cm^{-3}. Here 5×10^{22} cm^{-3} is simply the atomic density of pure Si, and Δ is the energy of substitution per atom. The energy of an isolated substitutional C impurity in Si is calculated to be $\Delta=1.6$ eV; see Table I.

Bean and Newman[7] reported an energy of C in Si of 2.3 ± 0.3 eV. The discrepancy of 0.7 eV with the present results would be considered acceptable even for a first-principles calculation. However, 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}. Although this result is still cited as the definitive measurement of carbon solubility, I know of no discussion of the unexpectedly large prefactor.

The actual measured solubility at high temperature (where the measurement should be most reliable), in combination with the theoretical prefactor, yields an energy of substitution of 1.7 eV, in good agreement with the present theoretical result. Moreover, the resulting solubility curve lies within the scatter of the experimental data over the entire temperature range, and actually improves the fit in the more reliable high-temperature range.

It therefore seems reasonable to propose a tentative reinterpretation of this experiment, as consistent with a solubility of $5\times10^{22}\exp(-1.7\text{ eV}/kT)$ cm^{-3}. In fact, an earlier experiment by Newman and Wakefield[4] was interpreted[8] as giving an energy of substitution of 1.5 eV, in excellent agreement with the present result of $\Delta=1.6$ eV.

The calculated interaction between substitutional carbons is repulsive, with first- and second-neighbor interaction energies of 1.3 and 0.3 eV, respectively. Thus precipitation of substitutional carbon is not expected in the absence of structural defects which could relieve strain.

Substitutional C is found to have a more complex interaction with the Si vacancy. The "nearest-neighbor" interaction, i.e., for C on one of the four threefold sites, is repulsive: 0.2 eV. The C dangling-bond energy is of the order of 1 eV larger than that for Si,[9] which would imply a 1-eV repulsive interaction with the vacancy. However, this is largely cancelled by the energy gained from partial relief of the strain, when the C sits on the less-constrained threefold-coordinated site.

The second-neighbor interaction between substitutional C and the vacancy (shown in Table I) is, however, attractive: -0.3 eV. This binding results simply from the partial release of strain, because the vacancy's neighborhood is more easily deformed than the perfect crystal. This result suggests how defects such as internal surfaces, where steric constraints are weakened, can serve as centers for the nucleation of SiC precipitates.

From Table I, the lowest-energy C defects in Si, after the substitutional, are the low-coordination interstitials: the (100) split interstitial, and after that the bond-centered interstitial. The structures of these defects are shown in Fig. 1. (The tetrahedral interstitial is calculated to have an even smaller energy; however, this is apparently[13] an artifact of the short cutoff.)

The formation energy for an interstitial, starting from a substitutional C, from Table I is $4.6-1.6=3.0$ eV. This is less than the calculated energy of any Si self-interstitial.[3] Thus Si self-interstitials (e.g., generated by irradiation) should react with substitutional C in an exothermic "kick-out" process, forming interstitial C in the

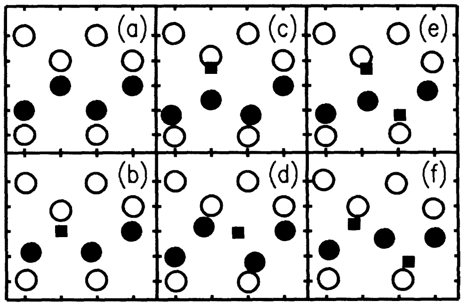

FIG. 1. Relaxed structure of selected C defects in Si. A $(1\bar{1}0)$ plane is shown, with the vertical and horizontal axes corresponding to the [001] and [110] directions, respectively. Each figure is 8×8 Å^2. Axis tick marks are chosen to correspond to ideal positions of Si atoms. Solid symbols are atoms in the plane of the figure; each open symbol corresponds to two atoms out of the plane, one in front and one behind. Circles are Si, smaller squares are C. (a) Pure Si, for reference. (b) Substitutional C in Si. Note inward displacement of neighboring Si. (c) Interstitial C in (001) split configuration. (d) Interstitial C in bond-centered configuration. Note displacement of C from [111] axis connecting its two Si neighbors. (e) Complex of substitutional C and C split interstitial, denoted SCSC in Table I. (f) Complex of substitutional C and C bond-centered interstitial, denoted CSC in Table I.

(100) split configuration. This reaction has been observed experimentally by Watkins and Brower,[5] with the resulting C interstitials having the expected structure.

The migration energy of the C interstitial, as well as its formation energy, can be estimated from Table I, and compared with experiment. One typically assumes[1] that the saddle point for interstitial migration is the next higher-energy interstitial configuration, in this case the bond-centered interstitial, giving a migration energy of $5.3-4.6=0.7$ eV. However, the split and bond-centered interstitials are both found to be (meta)stable minima, not saddle points, so the calculated migration energy should be >0.7 eV.

Watkins and Brower[5] have measured the interstitial migration barrier as 0.9 eV. This is consistent with the calculation if the barrier between the split and bond-centered interstitials is 0.2 eV. In fact, Song *et al.*[6] have studied a closely analogous system, the two-C substitutional-interstitial complex, and find precisely this behavior. Both the split and bond-centered configurations are found to be (meta)stable, with a barrier of 0.2 eV between them. This consistency provides strong, though indirect, evidence that the difference between split and bond-centered interstitial energies in Table I is rather accurate.

It is worth noting that in first-principles calculations of bond-centered interstitial energies, it is often found necessary due to practical constraints to consider only symmetry-preserving relaxations.[1] However, such a calculation for C in Si gives a formation energy of 6.6 eV, 1.3 eV higher than the value in Table I. Such a large value would qualitatively alter the conclusions for interstitial migration.

To address the formation energy of the split interstitial, we note that the activation energy for diffusion should be the sum of the formation energy of the interstitial from the substitutional, $4.6-1.6=3.0$ eV, plus the interstitial migration energy, 0.9 eV, giving a diffusion activation energy of 3.9 eV. This is in rather satisfactory agreement with the experimental value[4] of 3.1 eV. (Even first-principles defect calculations quote uncertainties of 0.5 eV or more.)

A powerful tool in identifying defects of low symmetry is the analysis of their stress-induced alignment. This alignment gives information on the elastic coupling tensor, $B_{ij}=dE/d\epsilon_{ij}$, or more precisely, on its traceless part $A_{ij}=B_{ij}-\frac{1}{3}\delta_{ij}\mathrm{Tr}B$. For the C interstitial, Watkins and Brower[5] found that $A_{11}=7$ eV, $A_{22}=0$ eV, and $A_{33}=-7$ eV. (Other elements are zero by symmetry.) Using the same orientation convention, the calculated components are $A_{11}=8$ eV, $A_{22}=-1$ eV, and $A_{33}=-7$ eV, in good agreement with experiment. (Even the agreement for A_{22} should be considered good, since the relevant energy scale here is 7 eV. It is fortuitous that subtracting the hydrostatic component results in a number near zero.)

Finally, we consider the interaction of interstitial C to substitutional C. Table I gives the energies of several intuitively reasonable configurations for the substitutional-interstitial complex, based on the low-energy split and bond-centered interstitials.

The labeling of the two-carbon complexes in Table I is intended to be intuitive. For the bond-centered case, the interstitial atom is bonded to two neighbors. The label indicates the atoms along the chain, with S for silicon; e.g., CSC means a Si interstitial bonded to two C, as in Fig. 1(f). The split interstitial has two central atoms, each threefold coordinated. The label *WXYZ* means that the two central atoms are *X* and *Y*; *W* is C if any neighbor of *X* besides *Y* is carbon, otherwise it is S. Thus SCSC means that the two central atoms are C and Si, the C has all Si neighbors, while the Si has two C neighbors (and one Si), as in Fig. 1(e).

From Table I, three of the complexes have calculated energies distinctly lower than the rest, with about 1 eV binding energy. The two lowest-energy defects, labeled SCSC and CSC, have been identified by Song *et al.*[6] as the two configurations of a bistable complex, with nearly identical energies, in agreement with the calculation. The defect structures are shown in Figs. 1(e) and 1(f). The third low-energy configuration, SCCS, has not been observed.

The strong binding of interstitial C to substitutional C can be easily understood as arising (at least in part) from the relief of stress. The split and bond-centered interstitials are both under considerable compression, $\frac{1}{3}\mathrm{Tr}B=-8$ and -18 eV, respectively. In contrast, substitutional C, being smaller than Si, is under a large tensile stress of 16 eV. The interstitial and substitutional can bind in complexes with much smaller stress than the individual defects, since the stresses are of opposite sign and tend to cancel. For the complexes labeled SCSC and CSC in Table I, the calculated stresses are only 8 and 12 eV, respectively.

In conclusion, by calculating the energies of a large number of possible C defects, we provide an overview of the expected properties of C in Si. The resulting picture is in excellent accord with a wide body of experimental data, including defect structures and reactions, activation energies for diffusion and for interstitial migration, and even the elastic coupling tensor for the low-symmetry C interstitial. For the solubility of C in Si, where a modest discrepancy exists with experiment, we propose that the experimental data can be more consistently reinterpreted as supporting the results of the present work.

It is a pleasure to acknowledge P. M. Fahey for helpful discussions, and R. M. Tromp for comments on the manuscript. This work was supported in part by ONR Contract No. N00014-84-C-0396.

---

[1] See, for example, R. Car, P. J. Kelly, A. Oshiyama, and S. T. Pantelides, Phys. Rev. Lett. **52**, 1814 (1984); **54**, 360 (1985); G. A. Baraff and M. Schluter, Phys. Rev. B **30**, 3460 (1984); Y. Bar-Yam and J. D. Joannopoulos, Phys. Rev. B **30**, 2216 (1984); C. S. Nichols, C. G. Van de Walle, and S. T. Pantelides, Phys. Rev. Lett. **62**, 1049 (1989).

[2] For some reviews of recent work on C in Si, see, for example, *Oxygen, Carbon, Hydrogen, and Nitrogen in Crystalline Silicon,* edited by J. L. Mikkelsen, Jr., *et al.*, MRS Symposium Proceedings No. 59 (Materials Research Society, Pittsburgh, 1986).

[3] J. Tersoff, Phys. Rev. B **39**, 5566 (1989). For further details on the potentials for pure Si and pure C, see, respectively, J. Tersoff, Phys. Rev. B **38**, 9902 (1988), and Phys. Rev. Lett. **61**, 2879 (1988).

[4] R. C. Newman and J. Wakefield, in *Metallurgy of Semiconductor Materials,* edited by J. B. Schroeder (Interscience, New York, 1961), pp. 15 and 201.

[5] G. D. Watkins and K. L. Brower, Phys. Rev. Lett. **36**, 1329 (1976).

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

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

[8] Reference 7 reports that the analysis of data of Ref. 4 implies an energy of substitution of 1.5 eV.

[9] J. Bernholc, A. Antonelli, T. M. Del Sole, Y. Bar-Yam, and S. T. Pantelides, Phys. Rev. Lett. **61**, 2689 (1988).

[10] C. Wang, J. Bernholc, and R. F. Davis, Phys. Rev. B **38**, 12752 (1988).

[11] The parameters used here for carbon, in the potential and with the notation of Ref. 3, are as follows: $A=1544.8$ eV, $B=389.63$ eV, $\lambda=3.4653$ Å^{-1}, $\mu=2.3064$ Å^{-1}, $\beta=4.1612\times10^{-6}$, $n=0.99054$, $c=19981$, $d=7.0340$, $h=-0.33953$, and $\chi=0.9972$. As discussed in J. Tersoff, Phys. Rev. B **37**, 6991 (1988), and in Ref. 3, the parameters R and S were not systematically optimized, a significant shortcoming of the present approach; instead, an abrupt cutoff $R=S=2.5$ Å was used for both C and Si, as discussed in the text.

[12] C. Kittel and H. Kroemer, *Thermal Physics* (Freeman, San Francisco, 1980), 2nd ed. [Equation (86) on p. 80 should be rederived using (80) rather than (83) to avoid the erroneous factor of e^{-1}.] This simple result is valid for substitutional impurities in the limit of low concentration, neglecting vibrational effects.

[13] As discussed elsewhere (Ref. 11), the somewhat arbitrary cutoff with distance is the most problematic aspect of the present potential. In the ideal tetrahedral interstitial, the second neighbors are only 15% more distant than the first neighbors, which creates particular problems. Increasing the cutoff to 2.9 Å raises the energy of the tetrahedral interstitial to over 10 eV; no other defect is affected even by the same order of magnitude by the cutoff. One can therefore only say that the energy should be between 3 and 10 eV, and is thus probably much larger than for the low-coordination interstitials.