

Magic numbers for vacancy aggregation in crystalline Si

D. J. Chadi and K. J. Chang

Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, California 94304

(Received 14 December 1987)

The stability of small n -atom vacancy clusters V_n in Si is examined for $n \leq 12$. The most stable structures occur for ringlike V_6 and "adamantine cage" V_{10} clusters and the least stable ones for V_5 and V_8 clusters. Electron-paramagnetic-resonance measurements are shown to provide strong support for the assignment of V_{10} to the dominant P_1 paramagnetic center in neutron- or ion-bombarded Si.

I. INTRODUCTION

Vacancies are the dominant intrinsic defects in many materials at high temperatures. Vacancies can also be created under nonequilibrium conditions by irradiation with high-energy photons, electrons, neutrons, or ions. Electron-paramagnetic-resonance (EPR) measurements and their analyses have been instrumental in identifying the nature of vacancy complexes in many semiconductors.¹ Silicon has been one of the most extensively studied systems¹⁻⁶ and many of the structural and electronic properties of its vacancy complexes have been deduced from analyses of EPR data.⁷ In the last few years a number of self-consistent calculations⁸⁻¹² on the elemental single-vacancy defect in Si have produced a clearer picture of the energetics, structural, and electronic properties of this defect. Not as much theoretical work has been done on multiple defects such as vacancy clusters.

This paper addresses primarily the problem of the structure and energetics of multivacancy structures in bulk crystalline Si. The vacancy-vacancy binding energy as a function of the size and shape of a vacancy cluster V_n is estimated and it is shown that particularly stable configurations consisting of six- and ten-vacancy aggregates can be obtained. A ten-atom vacancy cluster, instead of a nonplanar pentavacancy cluster,⁶ is proposed to be the source of the P_1 paramagnetic center in ion-bombarded Si.

The question of the extra stability of vacancy aggregates V_n at special "magic" numbers is very similar to that for Si_n clusters,¹³ where photofragmentation spectra¹⁴ show peaks in the yield for well-defined values of n . The most important difference between the two problems is that the crystalline structure of the lattice imposes severe restrictions on the shape of a V_n cluster, whereas the structure of a Si_n cluster need not have any resemblance to structural units in the bulk. This feature tremendously simplifies the problem for vacancies. Since bond energies in Si are much larger than typical atomic relaxation energies, the minimum-energy configuration for a multivacancy structure is generally the one that leads to the lowest number of dangling bonds. The consequences of this approach are examined in the following.

II. TOTAL ENERGY OF VACANCY CLUSTERS

The electronic and structural properties of an isolated vacancy have been examined in detail via *ab initio* self-consistent techniques.⁸⁻¹² The calculations show that the charge state of the vacancy depends on the position of the Fermi energy E_F inside the gap.⁹⁻¹¹ The neutral vacancy is the lowest in energy when E_F is more than 0.1 eV above the bulk valence-band maximum and the V^{2+} is the stable charge state at lower values of E_F . The V^- state becomes stable for E_F very close to the conduction-band minimum.¹¹ Here we consider only neutral vacancies. Ignoring lattice-relaxation effects for the moment, the formation energy E of a V_n vacancy cluster is approximately equal to

$$E \simeq \frac{1}{2} N_{DB} E_{\text{bond}}, \quad (1)$$

where N_{DB} is the total number of dangling bonds created by V_n and $E_{\text{bond}} \simeq 2.35$ eV is the energy of a Si—Si bond. The factor $\frac{1}{2}$ in Eq. (1) appears because every two dangling bonds can be considered to result from one broken Si—Si bond. For the case of an isolated neutral vacancy, the formation energy is therefore approximately equal to the cohesive energy of Si or 4.7 eV. This is close to the results of self-consistent calculations which show a formation energy of $\simeq 5 \pm 0.5$ eV.¹¹ A calculation based on the empirical tight-binding method¹⁵ with a single vacancy in a 64-atom $2 \times 2 \times 2$ cubic cell gives a value of 4.94 eV for the vacancy-formation energy. These results show that, at least for the case of the monovacancy, Eq. (1) gives a formation energy which is within 6% of more accurate estimates.

We now consider the binding of two neutral vacancies to form a divacancy. The number of dangling bonds for a divacancy is 6, as compared to 8 for two isolated vacancies. This indicates, therefore, a binding energy of E_{bond} for the divacancy. In general, for an n -atom vacancy cluster with N_{DB} dangling bonds, the total binding energy (E_B) relative to n isolated vacancies is

$$E_B(n) = \frac{1}{2}(4n - N_{DB})E_{\text{bond}}. \quad (2)$$

Because of the neglect of atomic relaxations, Eq. (2) generally overestimates the binding energy of vacancies. If

the relaxation energy is assumed to be proportional to the number of broken bonds, then $E_B(n)$ has the *same* form as that given in Eq. (2) but with E_{bond} replaced by E_{bond}^* , where $(E_{\text{bond}} - E_{\text{bond}}^*)$ is a measure of the relaxation energy. The calculated 0.6-eV relaxation energy for a monovacancy¹⁰ indicates that $E_{\text{bond}}^* \approx E_{\text{bond}} - 0.3$ eV. Relaxation effects make a small correction, therefore, to the energetics of vacancy formation in Si and, to a first-order approximation, this correction can be accounted for by a simple 13% renormalization of the bond energy E_{bond} .

The binding energy $E_B(n)$ in Eq. (2) tends to increase with the number of vacancies, n . If the vacancies make a chainlike structure with no closed loops of atoms, then the addition of each vacancy to the chain increases the number of dangling bonds, N_{DB} , by 2. The attachment of an isolated vacancy with four broken bonds to a chain results, therefore, in a net reduction of the dangling-bond number. From Eq. (1) the total energy of a chain with $N_{\text{DB}} = 2n + 2$ dangling bonds varies with n as

$$E(n) = (n + 1)E_{\text{bond}}, \quad (3)$$

and from Eq. (2) the binding energy varies as

$$E_B(n) = (n - 1)E_{\text{bond}}. \quad (4)$$

No magic numbers signaling uniquely stable structures occur in this situation. The binding energy of an isolated vacancy to a chain is independent of the number of vacancies already in that chain, so there is no preference for any particular V_n . An equivalent way of stating this is that the energy difference Δ_n defined as

$$\Delta_n = E(n) - E(n - 1) \quad (5)$$

is a constant independent of n for a chain of vacancies. The situation becomes very different when the vacancies

are allowed to assume configurations which close on themselves, e.g., rings in two dimensions or closed surfaces in three dimensions. In crystalline Si such configurations are not possible for $n < 6$ (see Fig. 1). A peak in Δ_n as a function of n is not by itself sufficient to assure the stability of a cluster. The stability also depends¹⁶ on the sign of the second-order energy difference ζ_n defined as

$$\begin{aligned} \zeta_n &= \Delta_{n+1} - \Delta_n \\ &= (E_{n+1} + E_{n-1}) - 2E_n. \end{aligned} \quad (6)$$

When ζ_n is *positive*, the dissociation reaction $2V_n \Rightarrow V_{n+1} + V_{n-1}$ is energetically unfavorable; when it is negative or zero the reaction is either exothermic or does not cost any energy.

III. RESULTS

The number of dangling bonds, N_{DB} , the total energy E for vacancy formation, the average binding energy per vacancy, $E_B(n)/n$, and the energy difference ζ_n are shown in Table I for $n \leq 12$ (with all energies given in units of E_{bond}). It can be seen that the most stable structures with $\zeta = 1$ occur for the $n = 6$ and 10 clusters shown in Fig. 1, while the least stable ones with $\zeta = -1$ occur for the $n = 5$ and 8 clusters. The other clusters have $\zeta_n = 0$ and are not particularly stable against dissociation. The average binding energy per vacancy has a small peak at $n = 10$, providing further evidence for the extra stability of the "adamantine cage" structure¹⁷ for the V_{10} cluster. The instability of V_5 and V_8 result from the fact that in each case the addition of a single vacancy to these clusters leads to the creation of a closed loop with no increase in the number of dangling bonds. The extra stability of

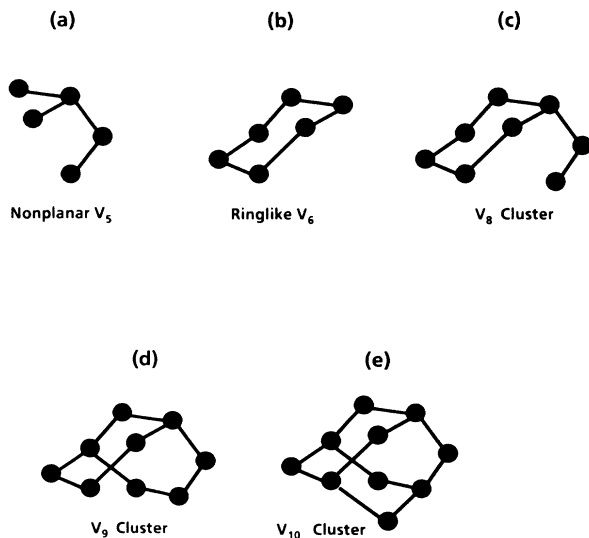


FIG. 1. Some vacancy clusters V_n with $n = 5, 6, 8, 9$, and 10 are shown in (a)–(d). The most stable clusters for $n \leq 12$ are V_6 and V_{10} and the least stable ones are V_5 and V_8 . There are many energetically degenerate configurations for V_5 and V_8 .

TABLE I. The number of dangling bonds, $N_{\text{DB}}(n)$, formation energy $E(n)$, average binding energy per vacancy, $E_B(n)/n$, and second-order energy difference ζ_n defined by Eq. (6) as a function of cluster size n is shown. All energies are in units of $E_{\text{bond}} \approx 2.35$ eV in Si. The most stable clusters with $\zeta_n = +1$ occur for $n = 6$ and 10 (see Fig. 1) and the least stable ones with $\zeta_n = -1$ occur for $n = 5$ and 8.

Cluster size	$N_{\text{DB}}(n)$	$E(n)$	$E_B(n)/n$	ζ_n
1	4	2		
2	6	3	$\frac{1}{2}$	0
3	8	4	$\frac{2}{3}$	0
4	10	5	$\frac{3}{4}$	0
5	12	6	$\frac{4}{5}$	-1
6	12	6	1.00	+1
7	14	7	1.00	0
8	16	8	1.00	-1
9	16	8	1.11	0
10	16	8	1.20	+1
11	18	9	1.18	0
12	20	10	1.17	

V_{10} can be attributed to the formation of *two* extra six-membered loops upon the addition of a vacancy to the V_3 cluster (see Fig. 1). For each V_n in Table I and in Fig. 1 the configuration with the smallest number of broken bonds has been used. In some cases (e.g., for V_5 and V_8) there are more than one such configuration. The V_{10} cluster corresponds to a small microvoid. Its stability results from the large degree of edge sharing between six-fold loops of broken bonds. A preliminary study indicates that the next larger magic number at $n = 14$ also consists of adamantine units, in this case two face-sharing cages.

The relatively large sizes of the most stable vacancy clusters raises the question of whether such structures can possibly occur in the bulk as a result of vacancy-vacancy collisions. The single vacancy is known to diffuse very rapidly in the bulk.⁹ The divacancy, however, is thought to be immobile because of the large activation barrier involved in the bond breakings needed to move it. At low concentrations and temperatures, therefore, single vacancies will either move to the surface or combine to form divacancies. Larger-sized vacancy clusters can, however, occur as a result of bombardment by high-energy ions or neutrons. The dominant P_1 paramagnetic center in neutron-irradiated Si has been attributed to vacancies. Lee and Corbett⁶ have suggested that the nonplanar V_5 vacancy cluster shown in Fig. 1(a) is the source of this center in Si. Their detailed analysis of electron-paramagnetic-resonance data⁷ in neutron irradiated Si indicate that the defect has the following properties: (i) It has equal numbers of V- or Λ -shaped missing links along the [110] and $[\bar{1}10]$ directions and is, therefore, nonplanar, (ii) its g tensor is very nearly [111] axially symmetric, and (iii) it is stable at temperatures up to 450°C as compared to 250°C for tetravacancy and 350°C for divacancy defects. These conditions on the P_1 center are better satisfied by the V_{10} adamantine structure than the nonplanar pentavacancy geometry. In particular, V_{10}

has equal numbers of V and inverted- V links along the [110] and $[\bar{1}10]$ axes, and unlike the V_5 cluster it is [111] axially symmetric. In addition, as discussed above five- and eight-atom vacancy clusters are expected to be the *least* stable aggregates and likely to dissociate at moderately high temperatures. The average binding energy per vacancy of $1.2E_{\text{bond}}$ for V_{10} is significantly larger than $0.80E_{\text{bond}}$ for V_5 and $0.75E_{\text{bond}}$ for V_4 , providing a more satisfactory explanation of its unusual stability at higher temperatures.

IV. CONCLUSIONS

In conclusion, the stability of vacancy aggregates in crystalline Si (c -Si) was examined. Six- and ten-atom vacancy clusters are found to be particularly stable and V_{10} is proposed to be the source of the P_1 paramagnetic center in neutron-irradiated Si. The stability of vacancy clusters V_n as a function of n should be very different in amorphous Si (a -Si) as compared to the crystalline case. This is related to the different ring statistics in a -Si. It is commonly believed that a -Si contains a large number of five- and sevenfold rings of bonds in addition to the usual sixfold rings of c -Si. Pentavacancies may be, therefore, as common as V_6 in ion-bombarded a -Si. Another area where magic numbers similar to that for vacancies may be expected is in dilute $A_{1-x}B_x$ alloys, where $x \ll 1$. If the B - B bonding is stronger than the A - B bonding, then the tendency of the B atoms to aggregate (which is opposed by the entropy of mixing) is further enhanced by the formation of magic-sized clusters.

ACKNOWLEDGMENTS

We would like to thank Professor M. L. Cohen and Dr. Noble Johnson for useful discussions. This work is supported in part by the U.S. Office of Naval Research through Contract No. N00014-82-C-0244.

¹J. W. Corbett, R. L. Kleinhenz, and N. D. Wilsey, in *Defects in Semiconductors*, Vol. 2 of *Proceedings of the Materials Research Society*, edited by J. Narayan and T. Y. Tan (North-Holland, Amsterdam, 1981), pp. 1-19.

²G. D. Watkins, *J. Phys. Soc. Jpn. Suppl. II* **18**, 22 (1963).

³G. D. Watkins and J. W. Corbett, *Phys. Rev.* **138**, A543 (1965); J. W. Corbett and G. D. Watkins, *ibid.* **138**, A555 (1965).

⁴J. W. Corbett, J. C. Corelli, U. Desnica, and L. C. Snyder, *Mater. Res. Soc. Symp. Proc.* **46**, 243 (1985).

⁵G. D. Watkins, in *Deep Centers in Semiconductors*, edited by S. T. Pantelides (Gordon and Breach Science, New York, 1986), p. 147.

⁶Y. H. Lee and J. W. Corbett, *Phys. Rev. B* **9**, 4351 (1974); **8**, 2810 (1972).

⁷M. Nisenoff and H. Y. Fan, *Phys. Rev.* **128**, 1605 (1962); W. Jung and G. S. Newell, *ibid.* **132**, 648 (1963).

⁸J. Bernholc, N. O. Lipari, and S. T. Pantelides, *Phys. Rev. B* **21**, 3545 (1980).

⁹G. A. Baraff, E. O. Kane, and M. Schlüter, *Phys. Rev. Lett.* **37**, 1504 (1979).

¹⁰G. A. Baraff, E. O. Kane, and M. Schlüter, *Phys. Rev. B* **21**, 5662 (1980).

¹¹R. Car, P. J. Kelly, A. Oshiyama, and S. T. Pantelides, *Phys. Rev. Lett.* **52**, 1814 (1984).

¹²R. W. Jansen and O. F. Sankey, *Phys. Rev. B* **36**, 6520 (1987).

¹³D. Tomanek and M. A. Schlüter, *Phys. Rev. Lett.* **56**, 1055 (1986); *Phys. Rev. B* **36**, 1208 (1987).

¹⁴L. A. Bloomfield, R. R. Freeman, and W. L. Brown, *Phys. Rev. Lett.* **54**, 2246 (1985).

¹⁵D. J. Chadi, *Phys. Rev. B* **25**, 785 (1984).

¹⁶W. D. Knight, K. Clemenger, A. A. de Heer, W. A. Saunders, M. Y. Chou, and M. L. Cohen, *Phys. Rev. Lett.* **52**, 2141 (1984).

¹⁷The adamantine structure corresponds to all the atoms, including all six face-centered atoms but excluding the eight corner atoms, in a unit cube of the diamond structure.