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Theory of Be-induced defects in Si

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The total energies and structures of a number of Be-induced defects in Si are investigated using *ab initio* local-density calculations. Our primary results are (1) the geometry of the isoelectronic center is found to correspond to a [111] substitutional-interstitial pair; (2) at normal doping temperatures the solubility of single Be interstitials is exceedingly low; (3) the low-energy defect spectrum includes large Be complexes containing at least one substitutional atom; and (4) the Be—Be bond in these larger complexes is metastable, while the Si—Be bond is stable for all defect configurations.

I. INTRODUCTION

If one attempts to dope Si with the group-II element Be one finds that only 10% of the Be atoms become electrically and optically active.[1] The purpose of this paper is to explain this intriguing behavior and, in particular, to find out why the remaining Be atoms are inactive. To accomplish this we use *ab initio* density-functional calculations to investigate the formation energies of a multitude of Be defect structures, ranging from the simplest monatomic defects to more complex defect clusters.

Experimentally it is known that the electrically active sites arise from substitutional double-acceptor Be dopants. Furthermore it is believed that the inactive defects are neutral Be pairs[2] that behave as "isoelectronic centers." The isoelectronic Be center in Si has been studied experimentally with infrared absorption,[3] photoluminescence,[4,5] Zeeman measurements,[6] and light absorption while under uniaxial stress.[7] From these studies the microscopic structure of the isoelectronic center was indirectly concluded to be either a substitutional-interstitial Be pair[2] or a Be pair occupying a single substitutional site (an "interstitialcy" or split interstitial).[4] Both configurations were proposed to be axially symmetric along the [100] axis.[4,6] In unpublished work, the experimental results from uniaxial stress[7] and Zeeman measurements[6] were reinterpreted and found to be consistent with a [111] symmetry axis.[8] A second isoelectronic center has also been seen in photoluminescence.[5] Electrical and optical studies of the Be *acceptor* centers in Si have been performed.[2,9,10] The total energies associated with some Be defects have been calculated previously.[11] The present work gives qualitatively different results compared to the latter as discussed below (see Sec. II).

The four major conclusions emerging from the present work are (1) the microscopic geometry of the isoelectronic center is found to be a [111] substitutional-interstitial Be pair; (2) the formation energy of interstitials is found to be high, thus the solubility of interstitials is exceedingly low; (3) among low-energy defects we find several "large" Be complexes; and (4) the bond strengths decrease in the order Si—Si, Si—Be and Be—Be. While the first two are always found to be stable, the Be—Be bond exhibits metastabilities as a function of charge state and the surrounding chemical environment.

The organization of our paper is as follows. In Sec. II we present the calculational method. Care has to be used when comparing total energies of differently charged defects, and our way of handling this problem is described in this section. In Sec. III results on single-atom Be-induced defects are reported. In Sec. IV we consider pair defects, in particular the isoelectronic center. We identify the microscopic geometry of this defect and characterize it by its local-mode frequencies and its corresponding first structurally excited configuration. In Sec. V we investigate the properties of larger Be defect clusters. We find that clusters with an *even* number of atoms are built up from isoelectronic pairs and have low formation energies. Other low-energy defects are clusters containing an *odd* number of atoms. Some interesting properties of the latter to emerge are the existence of a very-low-energy phonon mode and the possibility of metastable Be—Be bonds. In Sec. VI we summarize our results concerning the stability of the different types of bonds formed in Si:Be. From a knowledge of defect total energies we are able to explain the doping behavior of Si:Be and this is presented in Sec. VII. We speculate on generalizations of our results to other systems such as Si doped with group-VI elements in Sec. VIII. A summary is found in Sec. IX.

II. CALCULATIONS

The calculations were performed within the framework of density-functional theory using the local-density approximation and the pseudopotential approximation combined with the supercell method.[12] Further approximations involved truncations in the number of basis states used, selected summations over states in the Brillouin zone, and the finite size of the supercell. We checked the convergence with respect to these truncations.[13] The charged-defect calculations required extra care involving additional approximations and the procedure we followed will be described below in detail for the substitutional and interstitial Be sites. Finally, there is also the issue of band-structure shifts from one defect calculation to another, which will be discussed at the end of the section.

The substitutional Be atom has a doubly negative charge state associated with it. In order for the total energy not to diverge in the supercell method, each supercell must be constructed to be neutral. There are two ways to assure this neutrality. Either one includes the extra two holes in the calculation by removing two electrons in the highest occupied state, or one includes a constant neutralizing positive background charge. The first approach is preferred if the size of the supercell is large enough to contain the neutralizing, screened hole state. However, this is not the case for the supercell sizes at hand. Instead, the periodic repetition of defects forces the hole state to have a dispersion rather than being formed from states at the top of the valence band. In an eight-atom supercell this leads to errors as large as 1.4 eV for a Be *substitutional* defect. For *interstitial* Be, the inclusion of the neutralizing electrons at the bottom of the conduction band leads to a similar error. In addition these electrons will have the wrong energy due to the systematic band-gap underestimations present in the calculations. In the second approach, where a uniform neutralizing background charge is used, one needs to filter out unphysical effects caused by this background. To first order this can easily be done by simply subtracting out the Coulombic interaction of the neutralizing background with the charged defect. We have chosen the second approach and have included a neutralizing background in the charged-defect calculations. This was done by assuming that the charged-defect state had a size small compared to the supercell, allowing the Coulombic interaction to be approximated by that of a charged sphere with the supercell's volume and a point particle in the middle of the sphere with a charge appropriate to the defect. The corrections used for the 18- and 32-atom supercells were 0.5–0.6 eV for a doubly charged defect.

The band structures obtained for two distinct defect configurations may not be directly compared; i.e., the top of the valence band in one calculation is not necessarily aligned with the top of the valence band in another calculation. One needs to take this effect into consideration when comparing energies of differently charged defects. We see this effect, for example, for the Be substitutional defect, for which the top of the valence band was pushed up by the presence of the Be atom, while the bottoms of the conduction and valence bands remained relatively constant. For the nearest-neighbor substitutional pair defect the opposite was the case; the bottom of the valence band moved more than the top of the valence band. We chose to align both the top and bottom of the valence bands of different calculations to the Si bulk value. We averaged the two results and estimated the errors due to the alignment of the band structure to be the difference between the average and the extremes.

With the above considerations taken into account, our calculation was found to give different values of the total energies from the earlier calculation in Ref. 11. While they[11] calculate the energy difference between the neutral Be interstitial (Be_I) and substititional sites (Be_S) to be $E(\mathrm{Be}_I)-E(\mathrm{Be}_S)=0.2\pm0.3$ eV, we find a value of 2.4 ± 0.5 eV. We were able to reproduce their calculations and their results for an eight-atom unit cell and a 10-Ry energy cutoff, which were used in their calculation. We found that the total energy of the substitutional atom was 1.4 eV too high because of the inclusion of the hole states in the dispersive valence band. The total energy of the interstitial was 0.5 eV too low due to a partial cancellation of effects from dispersive electronic states and band-gap underestimation. We find further discrepancies for neutral defects that involve large lattice relaxations. Thus for the bond centered site versus the substititional-interstitial pair we calculate an energy difference of 2.7 eV, while they find 4.7 eV. This probably results from their use of a smaller supercell (eight or 16 atoms), which allows less room for atomic relaxation.

Finally, the formation energies are referenced to *c*-Si and metallic Be. In particular, the energy we quote for *n*-atom defects is the energy for *n* Be atoms to convert from Be metal to the specific configuration with any affected Si atoms going to a Si surface:

$$E_{\mathrm{form}}=E_{\mathrm{form}}[\mathrm{Si}_p\mathrm{Be}_n]-pE_{\mathrm{form}}[\mathrm{Si}]-nE_{\mathrm{form}}[\mathrm{Be}_{\mathrm{metal}}]\ .$$

III. SINGLE-ATOM DEFECTS

Our results for the Fermi-level-dependent energies of single substitutional and single interstitial Be defects are shown in Table I. There are two different interstitial positions, and we find that the tetrahedral site is preferred by about 0.5 eV. Relaxations are largest for the substitutional site, for which the Be—Si bond length (2.25 Å) is 4% shorter than the Si—Si bulk bond length [Fig. 1(a)]. The substitutional site is more stable than the interstitial site for most values of the Fermi level, except when it is close to the valence-band maximum. We could not identify any states in the gap related to either defect. This may be because the gap states one finds experimentally extend beyond the size of the supercell. The remaining one-atom defect is the bond centered site, in which two Si—Be bonds are formed [Fig. 1(b)]. We find that this site is energetically unfavorable.

We performed an investigation of the possibility of metastable states associated with a single substititional Be defect (Be_s). Figure 2 shows the total-energies path for a Be atom to move gradually from the initial Be_s position (at the origin) to the interstitial position (at a distance $d\sim2.5$ Å) at which point a Si vacancy is also created. At first no atomic relaxations were included. There are three curves corresponding to the Be atom moving away from the origin along the [111] axis being either positively or negatively charged, and moving away from the ori-

TABLE I. Energies of the isolated substitutional and interstitial defects in Si. The position of the Fermi level μ is calculated from the top of the valence band. The zero of energy is chosen to be the energy of Be in its metallic form.

Defect type	Energy
Substitutional	1.1 ± 0.5 eV-2μ
Tetrahedral interstitial	1.0 ± 0.2 eV$+2\mu$
Hexagonal interstitial	1.5 ± 0.2 eV$+2\mu$

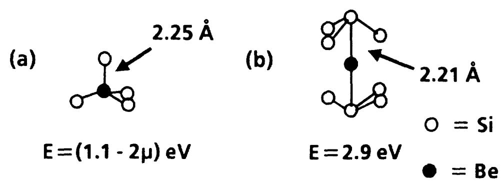

FIG. 1. Relaxed configuration and total energies of (a) substitutional and (b) neutral Be bond-centered defect. The solid circles represent the Be atoms and the open circles represent the Si atoms. The energy reference is bulk Si and metallic Be, and the reference for the Fermi level is the valence-band maximum.

gin along the [100] axis, being positively charged. We note that none of these curves indicate any metastability. We subsequently allowed relaxations for the ([111],+2) path, which is indicated with the unconnected points. We note that the force towards the origin *increases* slightly, further supporting the lack of a metastable state.

IV. PAIR DEFECTS.

A. The isoelectronic center

We considered several geometries for neutral Be pairs that could form an isoelectronic center. The corresponding local minima configurations we found are presented in Fig. 3(a)–3(e). We intentionally looked for defect geometries that would not preserve the bond topology of the Si lattice. For example, we initially started out the configurations in Figs. 3(a) and 3(c) as combinations of onefold-coordinated singly positively charged Be atoms and threefold singly negatively charged Be atoms. After relaxation, however, all but one configuration were determined by the Si lattice and thus were combinations of interstitials (Be_I) and substitutional (Be_S) sites. The one large lattice relaxation we found was for the two Be atoms occupying the substitutional site along the [100] symmetry axis [Fig. 3(e), a configuration which is referred to as an "interstitialcy," or split interstitial].

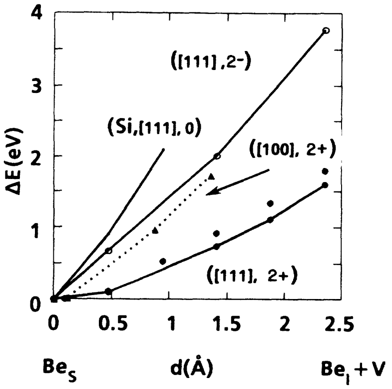

FIG. 2. Total energy E of a Be atom interacting with a Si vacancy at distance d. Results are shown for two different charge states (2+ and 2−) and two different incoming directions ([111] and [100]). The unconnected points represent the value of the energy after full relaxation of the (2+) charge state and the [111] incoming direction. For comparison the energy of a Si atom interacting with a vacancy (upper line) is also included.

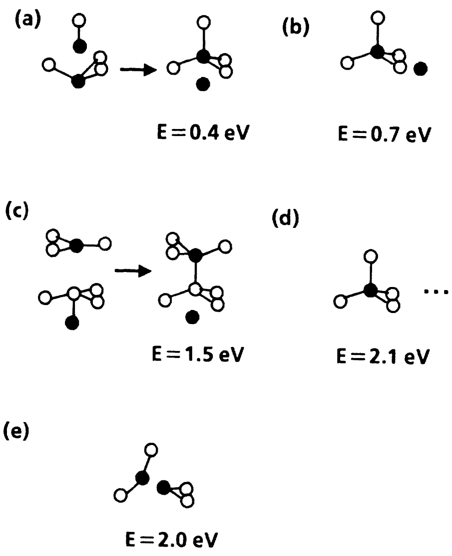

FIG. 3. Relaxed configurations and total energies of neutral Be-pair complexes. The error bars are 0.2 eV for configurations (a)–(c) and (e), and 0.5 eV for the configuration in (d).

In Fig. 3 we also present for the formation energies associated with the optimized configurations. The zero of energy is taken to be bulk Si and Be metal (the latter is relevant to the Be doping procedure discussed in Sec. VII). As we see, the most favorable configuration consists of a Be_I behind a Be_S in the [111] direction [Fig. 3(a)]. Note that the interstitialcy [Fig. 3(e)] is much higher in energy. This allows us to identify the isoelectronic center to be the substitutional-interstitial pair (SIP) in the [111] direction.

To characterize the [111] SIP we calculated some typical local-mode frequencies. We considered the modes associated with the isolated Be_I and Be_S defects as well as for the [111] SIP. The results are shown in Table II.[14] The substitutional defect gives rise to a vibration at 500 cm^{-1} and the interstitial gives a vibrational frequency at about 370 cm^{-1}. The substitutional vibration is consistent with the experimental finding of a (broad) band centered around 500 cm^{-1}. As we will explain later,

TABLE II. Calculated local-mode frequencies of the Be_S, Be_I, and (111) Be_I-Be_S pair.

Defect type	Local-mode frequency (cm^{-1})
Substitutional	500
Tetragonal interstitial	370
(111) Be_I-Be_S pair	860
	310

there might be only a few isolated interstitials present in the p-doped materials studied, making the vibration of 370 cm^{-1} very weak. For the [111] SIP we calculated the frequencies of two [111] modes of vibration, the symmetric and antisymmetric Be-Be states.[15] Our results are 860 and 310 cm^{-1}, respectively. They can be considered symmetric and antisymmetric combinations of the isolated Be_S and Be_I frequencies. The higher frequency should be very characteristic in absorption measurements but this part of the spectrum has thus far not been examined.

The [111] symmetry of our lowest-energy configuration is in contrast to the earlier experimental interpretation that the symmetry should be [100].[4,6] However, it is consistent with Zeeman experiments,[6] in that the Zeeman splittings were found to be simplest for the [111] direction. It is also consistent with data on the uniaxial stress dependence of the low-temperature luminescence[7,16] that shows that the symmetry axis is the [111] axis.[8]

Isoelectronic defects like the SIP perturb the Si lattice and can trap electrons and holes. Depending upon the structure of the perturbation, the electrons and holes will be trapped with different strengths. Thus one can classify isoelectronic centers as "acceptorlike" or "donorlike"; i.e., if the electron is trapped first and is bonded more tightly, the center obtains an acceptorlike character, and vice versa. The Be center was initially characterized as donorlike,[4] but later it was determined to be acceptorlike.[3,7] The experimental finding that the isoelectronic center is acceptorlike can be rationalized as follows: In the SIP, a short-range dipole potential results from a doubly negative-charged substitutional Be atom and a doubly positive-charged interstitial Be atom. The positive potential is deeper and more localized than the negative potential since it results from an atom stripped of its electrons (the interstitial) rather than the forming of delocalized bonds (the substitutional). Thus the total potential would bind an electron more tightly than a hole, giving the acceptorlike behavior.

It is interesting to ask how the [111] SIP relates to the other SIP's of Fig. 3. Due to the absence of large lattice relaxations, the energetics of the configurations are governed simply by the Coulombic interaction. In Fig. 4 we have plotted the total energy versus distance between the Be_S and Be_I atoms. We see that the energy decreases with distance and we note that the configuration with the lowest energy (SIP [111]) is the configuration which allows for closest approach when we take into account the steric effects of the surrounding network of bonds (the calculated distance is 1.9 Å). By comparing the energy of the [111] SIP with the energy of separated substititional and interstitial defects from Table I we find an electrostatic binding energy of about 1.7±0.5 eV making the interstitial and substititional Be atoms tightly bound.

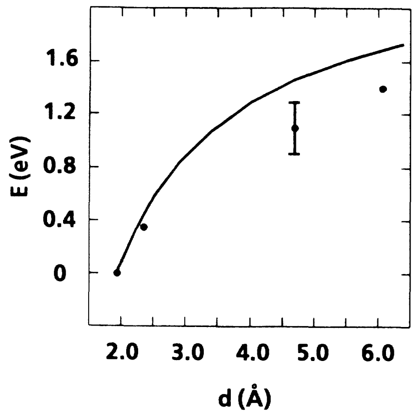

FIG. 4. Energy per atom of interstitial-substitutional Be pairs as a function of separation. The lowest-energy structure is the [111] SIP. A $1/d$ curve is included as a guide to the eye.

Let us finally focus on the relationship of the [111] SIP and the first structural excitation. These are related by changing the interstitial site from the nearest-neighbor-tetrahedral site (along the [111] direction, Fig. 3(a)) to the second-nearest-neighbor tetrahedral site (along the [100] direction, Fig. 3(b)). A second, weaker, isoelectronic binding center that may correspond to the [100] pairing has been seen in experiment. The frequency of the corresponding luminescence is lower than for the main center,[5] which is consistent with the smaller Be-Be interaction of the [100] SIP. We calculated the barrier between the two SIP states as shown in Fig. 5. We are able to give an upper and a lower bound on the barrier height of 0.4±0.2 and 0.8±0.2 eV (corresponding to the open and solid circles in Fig. 5, respectively).[17] This barrier can be rationalized as follows: between the [111] and [100] configurations lies the hexagonal interstitial site. In pure Si, this site is higher in energy that the tetrahedral interstitial site by about 0.5 eV (see Table I). The existence of the barrier suggests that one can alter the fraction of SIP's in [111] and [100] configurations by changing the annealing procedure. In a related, weakly interacting system, Al_S-Fe_I pairs in Si, this has been demonstrated.[18,19]

B. Charged-defect pairs

Calculations were performed on substitutional-substitutional and interstitial-interstitial pairs. The equi-

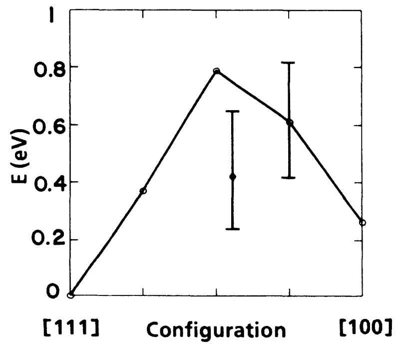

FIG. 5. Energy path going from the [111] paired configuration to the [100] paired configuration. The curve shows the energy associated with a linear, unrelaxed path, while the single solid circle is the point of maximum energy of a fully relaxed path.

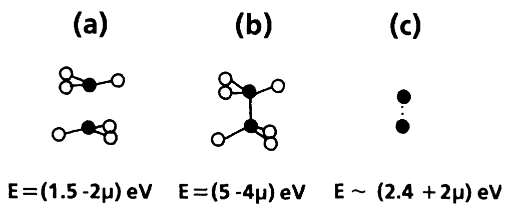

FIG. 6. Relaxed configurations and total energies of charged Be pairs. Note that our results for the interstitial pair show that the Be—Be bond is weak (symbolized with a dotted line).

librium configurations are shown in Fig. 6. There are two possible charge states for the substitutional pair, (2−) or (4−). In the former configuration the Be atoms are threefold coordinated with the Be—Be bond broken [see Fig. 6(a)]. The corresponding energy is similar to the energy of the isolated substitutional (see Table I). The (4−) charge state is high in energy and has both Be atoms four-fold coordinated [Fig. 6(b)]. Finally, our results for the interstitial-interstitial pair indicate that the interstitial-interstitial bond is not a particularly strong bond [Fig. 6(c)]. The Be-Be distance was increased from the ideal 2.35 Å value to 2.50 Å, and the highest filled state was conduction-band like.

V. LARGER Be COMPLEXES

Using our finding that the Si lattice dominates the bonding structure for Be defect pairs as well as for single-Be-atom defects, we can build defects of increasing complexity from combinations of simple substitutional and interstitial defects. Thus three-atom defects can be built from three substitutionals, one substitutional and two interstitials, two substitutionals and one interstitial or three interstitials; four-atom defects from four substitutionals, etc. To gain as much Coulombic energy as possible, these complexes should contain a balanced amount of substitutionals and interstitials and be compact.

We performed calculations on the three-atom geometries shown in Fig. 7. The neutral three-atom complex with the lowest total energy is the one consisting of two nearest-neighbor substitutional defects and an asymmetrically placed interstitial [Fig. 7(a)]. Let us examine this defect more closely. First, let us focus on the placement of the interstitial atom in the (111) plane. In Fig. 8(a) and 8(b) we are looking along the [111] axis. The atom in the middle is one of the two substitutional Be atoms, the second one is hidden behind. The directions of the Be—Si bonds are indicated. By symmetry, the Be_I atom is in one of two places: either it is positioned on one of the bonds [Fig. 8(a)] or between the bonds [Fig. 8(b)]. The position in between the bonds is a hexagonal interstitial, while the position on the bonds is a tetrahedral interstitial. The tetrahedral position is not as clear a favorite as for the isolated interstitial (Table I) because it is now a (1,1,1) position as compared to the upper Be_S but in the (1,0,0) position (which is less favored) as compared to the lower Be_S. Furthermore, the Be_s—Be_S bond is about 0.5 Å elongated, giving additional space for the hexagonal site and thereby lowering the total energy of that site. Our calculation indicates that indeed the tetrahedral position is still favored but by only 0.2 eV (our calculations further indicate that this energy difference is insensitive to [111] uniaxial strain). As the energy difference is very small there is a corresponding very soft phonon mode associated with it at 60–100 cm^{-1}. A second interesting feature of the three-atom complex in Fig. 7(a) is that by adding electrons one can make the Be-Be bond form. The corresponding charged configuration is shown in Fig. 7(b).

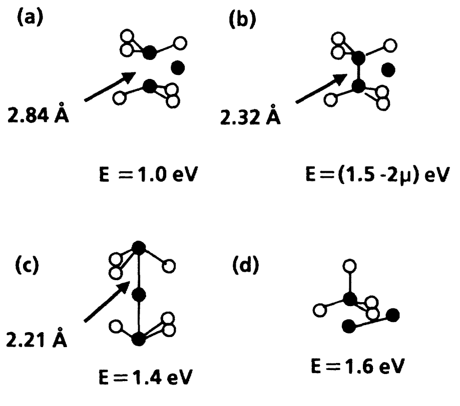

FIG. 7. Relaxed configuration and total energy of several three Be-atom complexes.

The third three-atom complex shown in Fig. 7(c) is of higher energy. This geometry is very similar to the Be bond-centered defect. Note that the energy of the bond-centered Be atom in the Be—Be bond is low compared to the bond-centered Be atom in the Si—Si bond. This is due to the Be—Be bond being much weaker and more easily deformed than the Si—Si bond. Finally, the

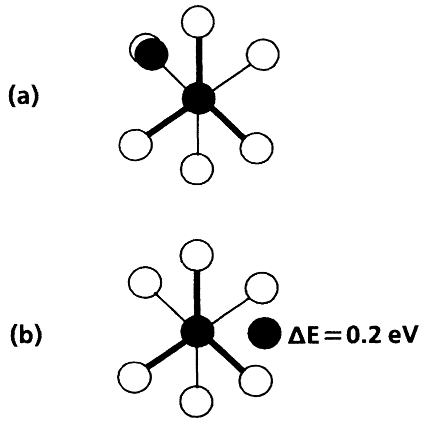

FIG. 8. Schematic drawing of the position of the interstitial atom in the neutral Be complex of Fig. 7(a). The view is along the [111] direction. There are two symmetry inequivalent positions for the interstitial: (a) the tetrahedral site or (b) the hexagonal site. The energy of the hexagonal site is about 0.2 eV higher.

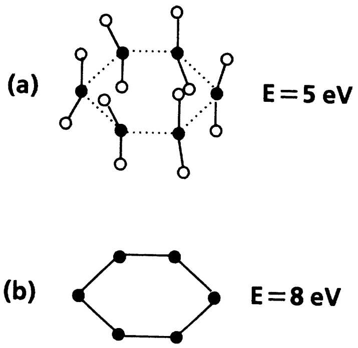

FIG. 10. Relaxed configurations and total energies of Be-atom six rings. (a) Substitutional ring; (b) interstitial ring.

configuration consisting of two interstitials and one substitutional is shown in Fig. 7(d). In comparison with the interstitial-interstitial pair, the distance between the two interstitials in Fig. 7(d) is smaller (2.31 Å). This results from the substitutional defect partially canceling the Coulombic repulsion between the interstitials, creating an "ionic" negative-U center.

The equilibrium geometries of the four-atom configurations we examined are shown in Fig. 9. Both are built from the three-atom defect in Fig. 7(a) by adding another interstitial atom. The configuration can relax in two directions. Either all the atoms involved are singly charged, in which case the Be—Be bond between the substitutional atoms is broken and a bond between the interstitials is formed, or the atoms are doubly charged, which means that the bond between the substitutional Be atoms is there, while the interstitials are not bonded. The configuration relaxes directly into the latter state, and we can think of the configuration as being built up from two [111] SIP's. These interact favorably through the dipoles formed. There are several ways that the two [111] dipoles can interact, the most energetically favorable should be when the dipoles are antiparallel [Fig. 9(b)]. We calculated the energy of this state as well and found, indeed, that it was the lowest. By extrapolation we anticipate that extended linear and planar configurations of the [111] SIP's may be of even lower energy.

Finally we considered two defect geometries consisting of six Be atoms aggregated in sixfold rings (Fig. 10). The ring can occupy either all substitutional sites [Fig. 10(a)], or all interstitial sites [Fig. 10(b)]. In the latter case the ring has been rigidly shifted to the "interstitial" lattice points and the bonds formed are Be—Be bonds rather than Si—Be bonds. In both geometries all the Be atoms are two-fold coordinated and neutral. Both configurations have high energies (5 and 8 eV).

VI. THE Be—Si AND Be—Be BONDS

Using our results we are able to compare the stability of Si—Be and Be—Be bonds. From Fig. 1 we see that the Si—Si bond is stronger than the Be—Si bond. Also we see that as we take out electrons from the system, the Be—Si bond becomes weaker but it persists. Indeed, for both monatomic defects and atom-pair defects we find the Be—Si bond to be stable. However, the Be—Be bond is not stable in isolation (there is no Be—Be molecule, presumably due to unreactive filled *s* states) and is weak in the solid. This is apparent from the defect configurations we have studied that include Be—Be bonds. These are summarized in Fig. 11. Here we see that the Be—Be distance changes as we change the number of neighboring interstitials and the amount of charge in the system. Thus while the (2−) configuration of two nearest-neighbor substitutional Be atoms [Fig. 11(a)] has a broken Be—Be bond (bond length of 3.10 Å), as we add one interstitial [Fig. 11(b)] the Be—Be distance decreases due to the mutual Coulombic attraction to the interstitial. This defect is neutral and has an empty state at 0.2±0.1 eV above the top of the valence band (translating to about 0.3 eV if we adjust for the band-gap error). The empty state is presumably associated with the weak Be-Be bonding state. As we fill this state the Be-Be distance decreases (to 2.32 Å) and a bond is formed [Fig. 11(c)]. If we add another interstitial to this configuration [Fig. 11(d)] the Be—Be bond further contracts (to 2.21 Å). A Be—Be bond can also form if we add two electrons to the isolated nearest-neighbor substitutional configuration [Fig. 11(e)]. Here the bond length is somewhat longer, 2.47 Å. Finally, the Be—Be bond is at best weak between two neighboring interstitial atoms [Fig. 11(f)].

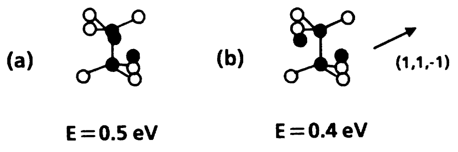

FIG. 9. Relaxed configuration and total energy of neutral four Be-atom complexes.

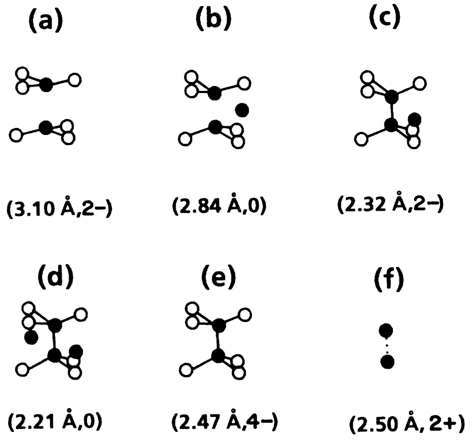

FIG. 11. Defect configurations and the corresponding Be-Be distances and charge states for defects examined.

VII. DEFECT ENERGIES AS A FUNCTION OF THE FERMI LEVEL AND THE DOPING BEHAVIOR

Figure 12 shows a diagram of the defect energies as a function of the Fermi-level position throughout the gap region. Let us consider the defect energies at ordinary doping conditions:[2] The temperature is about 1300 K, the Fermi level is at midgap, and Be metal is soldered to the Si sample. From Fig. 12 we find that the lowest-energy structures in the midgap region are the Be metal, the single or paired substitutional Be defects, the single or double [111] SIP's, and the charged three-atom complex from Fig. 7(b) (further low-energy extended defects may also be possible). The [100] SIP is also created, although it is not included in Fig. 12.

Most strikingly, the isolated single interstitial defect is 2 eV high in energy and should not exist in equilibrium. It enters the crystal and will remain only if it can rid itself of the extra energy by turning substitutional or by forming complexes. A similar situation occurs for Li interstitials in Ga-doped Si, for which the solubility increases rapidly with the Ga content.[20] The differences between Si:Ga,Li and Si:Be are threefold: First, the binding energy of the Be SIP is roughly four times larger due to the doubly charged Be$_I$ and Be$_S$ defects, preventing them from dissociating. Second, the process with which the interstitials are incorporated is separate from the process of substitutional incorporation for Si:Ga,Li but not for Si:Be. In the latter the Be atoms have a *simultaneous* dual role of Ga-like (Be$_S$) and Li-like (Be$_I$). Third, while Si:Ga,Li becomes fully compensated, Si:Be is only 90% compensated. One can speculate that the less-than-full compensation in Si:Be happens as follows: At the doping temperature, equilibrium concentrations are set up of all defect configurations. As the temperature is lowered, additional Be interstitials enter the sample and form tightly bound pairs with substitutional defects or become members of larger defect complexes. Subsequently, the layer adjacent to the doping metal will have accommodated a maximal number of interstitials preventing further Be interstitials from dissolving into the Si. The result is that the remaining substitutional Be atoms, deeper into the sample, are left uncompensated.

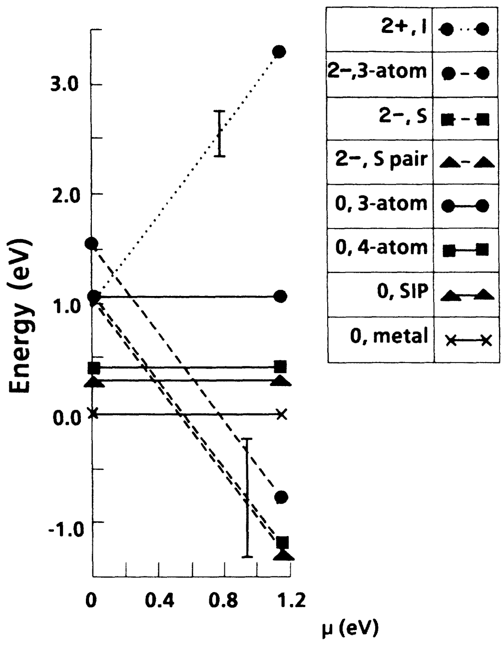

FIG. 12. Defect energies as a function of Fermi level. The zero of energy is taken to be Be in its metallic state. A guide to the figure is supplied in the upper right hand corner. It labels each curve with the charge state of the defect and the defect configuration. "2+,I" is the interstitial in the doubly charged state, "2−, 3-atom" is the doubly charged three-atom complex from Fig. 11(c), "2−, *S*" is the substitutional site in the doubly negative state, "2−, *S* pair" is the nearest-neighbor substitutional-substitutional pair, "0, 3-atom" is the lowest energy neutral three-atom cluster from Fig. 7(a), "0,4-atom" is the lowest energy four-atom cluster from Fig. 9(b), "0,SIP" is the [111] SIP, and "0, metal" is the energy of Be in its metallic form. The sizes of the error bars for the substitutional and interstitial defect energies are indicated.

VIII. POSSIBLE GENERALIZATIONS TO OTHER SYSTEMS

The Si dopants that could self-compensate in a manner similar to Be are group-II and group-VI elements[21]—the substitutional dopants (with charges 2− and 2+, respectively) can pair up with the interstitials (charges 2+ and 2−, respectively). In order for these to behave similarly to Be, one more condition must be met: they must preserve the bond topology of the Si lattice. Be dopants preserve the Si lattice for two reasons. First, the weakness of the Be potential allows Si with its much stronger potential to dominate the bond formation. Second, the size of the Be atom does not deviate much in the Si network (the Be—Si bonds are only 5% shorter than the perfect Si—Si bond). Zn has been found to be involved in an isoelectronic center,[22] as have S and Se.[19] In the case of Zn it has, however, not been ruled out that it pairs up with some other impurity (like Fe or Cu).[22]

We can speculate and generalize the *acceptorlike* behavior of the Be SIP to other neutral SIP systems. All which contain a positively charged interstitial (i.e., column-II dopants in Si) should be acceptorlike. This results from the positive interstitial potential being more localized than the negative potential of the substitutional defect. On the other hand, if the interstitial results from a negatively charged ion (i.e., column-VI element) we might predict a donorlike behavior. In the latter case, however, the two length scales (the ionic radius of the interstitial and half the substitutional bond length) become more alike and both the hole and electron may be equally tightly bound and the situation is more complex.

A parameter that enters into the doping behavior is the dopant-dopant bond strength. Between the group-II and group-VI dopants, the II-II bond strength is the weakest. Thus while for group-VI donors there is a tendency for pair formation of two substitutional defects and two interstitial defects,[19] this tendency is smaller for Si:Be. Furthermore, this weakness also introduces metastable behavior as one changes the charge state or the number of interstitials close to the Be—Be bond.

Our investigation has shown that the doping behavior of Be in Si is quite intricate, involving many different types of defects formed and possibly defects different from what earlier was proposed. It may be that this is a general phenomenon among dopant defects. Earlier works on group-VI donors have found that there exist a tendency for pair formation,[19] Li can form four-atom clusters,[23] and similarly for Si:H different defect pairs and even extended two-dimensional platelets have been found to exist.[24]

IX. SUMMARY

Be in Si is a double acceptor and as such has a relatively large perturbative charge deficiency. This prevents it from acquiring simple doping properties. Indeed, only a fraction of the Be becomes electrically active. In the paper we have shown that no single-atom configuration could account for this behavior, and we identified the lowest-energy Be *pair* geometry that would be inactive. It was determined to be a [111] substitutional-interstitial pair (SIP), and was characterized with its phonon frequencies and lowest structural excitation. It was found that the energy of this inactive pair was comparable to the energy of the active substitutional site at the relevant doping temperatures, possibly explaining its prevalence. Furthermore, larger Be-Be complexes (three and four atoms) were calculated to be energetically favorable as well. In addition, favorable dipole-dipole interactions may make extended defects possible. The uncompensated interstitial defect, however, had a high formation energy at doping temperatures. While the Coulombic interaction from the doubly charged Be atoms was large, the covalent Be—Be bond was found to be weak and metastable. Its stability depended upon the chemical environment as well as upon the Fermi level. The Si—Be bond was found to be completely stable.

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[14] The local-mode frequencies for the isolated defects were obtained by assuming that the surrounding Si atoms do not move appreciably. This is justifiable since the Be atom is lighter than the Si atom by a factor of 3. The Be atoms then moved in a tetrahedrally symmetric potential and the frequencies reported are associated with the lowest eigenmode. We performed a test calculation for the substitutional defect allowing one of the Si atoms to move. We found that this changed the local-mode frequency by 20 cm^{-1}.

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