# Rich chemistry of copper in crystalline silicon

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The interstitial copper ion ($Cu_i^+$) is a very fast-diffusing impurity in Si. While the isolated interstitial is a shallow donor, it reacts with impurities and defects and these reactions affect the electrical properties of the material. Copper passivates shallow acceptors, forms pairs with various impurities, including itself, and precipitates at defects. Some Cu precipitates are strong electron-hole recombination centers. In this paper, interstitial and substitutional copper, copper-acceptor pairs, and the precipitation of copper at a model nanodefect, the ring hexavacancy, are studied in clusters at the *ab initio* Hartree-Fock level. The chemistry of copper in Si is not as simple as commonly believed, even in the case of $Cu_i^+$. The interstitial ion is not in the $3d^{10}4sp^0$ configuration as often assumed, but transfers some electrons into the $4sp$ shell, which ultimately is responsible for the various covalent interactions between copper and its host crystal. In addition to energy-optimized configurations and binding energies, a number of details of the chemical interactions shed light on the behavior of copper in silicon. [S0163-1829(99)00232-5]

## I. INTRODUCTION

Copper is a common impurity in silicon. Its properties have been studied experimentally for many years.[1] Since several excellent reviews have recently been published,[2–4] this introduction is limited to the key issues directly relevant to this paper.

Interstitial copper is believed to be a shallow donor in Si, and exists almost exclusively as the positive ion $Cu_i^+$. Since it reacts with various impurities (including itself), its diffusion is trap limited. The first measurements[5] of the diffusivity of copper in Si found an activation energy of 0.43 eV, but the most recent value[6] $D=(3.0\pm0.3)\cdot10^{-4}\times\exp-(0.18\pm0.01)eV/k_BT$ (cm$^2$/s) shows that the activation energy is substantially lower. It is close to the 0.24 eV predicted by *ab initio* Hartree-Fock (HF) calculations[7] for the diffusion of $Cu_i^+$ along the interstitial tetrahedral–hexagonal–tetrahedral (T-H-T) path.

It may be a surprise that $Cu_i^+$—the heaviest transition metal (TM) ion in the $3d$ series—is such a fast diffuser while $Ti_i^+$—the lightest ion in the series—cannot be made to diffuse much at all up to the melting point of the material. The activation energy for diffusion of $Ti_i^+$, calculated[7] at the same level of theory as that of $Cu_i^+$, is 3.29 eV. The strength of the chemical interactions between various TM's and the Si host obviously varies considerably from one element to the other in the $3d$ series, and each of these elements must be studied in detail to understand the peculiarities of its interactions with the crystal.

The chemomechanical polishing of Si wafers with a slurry containing copper generates a rapidly-diffusing species $X$, which passivates shallow acceptors. $X$ was identified as Cu by Prescha *et al.*,[8] and Cu-acceptor pairs have been studied by several groups.[9–11] The dissociation energies are 0.61 eV for {Cu,B}, 0.70 eV for {Cu,Al}, and 0.71 eV for {Cu,Ga}. Copper also forms pairs[10,11] with TM's such as Pt or Au, with itself[12] (the substitutional–interstitial {$Cu_s$,$Cu_i$} pair), and other complexes still unidentified, all with dissociation energies of the order of the eV.[11,13] Copper weakly traps at or near interstitial O since the intrinsic diffusivity of $Cu_i^+$ below room temperature is higher in floating zone than in Czochralski Si.[3] Copper also interacts with common impurities such as C, P, As, and others. Abnormally high-annealing rates of divacancies ($V_2$) in samples with surface-deposited copper have been interpreted as being caused by the passivation of $V_2$ by copper.[14] Little is known about most of these interactions.

Finally, copper has a strong tendency to precipitate at defects such as dislocations,[15,4] grain boundaries,[16] nanocavities,[17–19] radiation-damaged regions,[20,21] stacking faults,[22] etc. Copper forms star-shaped etch pits, and platelets in {111} planes.[4] Such precipitates reduce the lifetime of charge carriers.[23,24] A range of gap levels observed by deep-level transient spectroscopy (DLTS) have been assigned to copper precipitates. These levels tend to form defect bands.[3,4]

Much of what is known about Cu in Si deals with large precipitates—visible for example by cross-sectional transmission electron microscopy or electron-beam induced current—or long-range interactions such as the dissociation of copper-acceptor pairs observed in transient-ion drift (TID) experiments. These types of experiments reveal little about the *local* (atomic-level) interactions. The microscopic nature of the interactions involving Cu in Si are poorly understood. Not surprisingly, most of the open questions are related to nearby interactions such as the following.

(1) If interstitial copper in Si is like the free ion, that is in the closed-shell $3d^{10}4sp^0$ configuration, why does it interact at all with impurities?

(2) What is the nature of Cu-acceptor interactions, and why is the dissociation energy of Cu-acceptor pairs so low? The binding energies of H-acceptor pairs are about twice larger.[25] The acceptor-dependence of these energies implies that the interaction is not purely Coulombic.

(3) What are the interactions between copper and lattice defects of nanometer size or larger? Where does Cu fit in a void, and what are the binding energies?

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(4) What is the origin of the electrical activity of copper precipitates?

This paper proposes answers to such questions on the basis of *ab initio* HF calculations in clusters. Such calculations have been used to predict the activation energy for diffusion[7] of $Cu_i^+$ and the structure of the passivated {Cu,B} pair.[26] Preliminary binding energies and configurations[27] confirm that the methodology is appropriate.

Except for these HF studies, the theoretical work published so far has dealt with the prediction of trends for *isolated* TM impurities at *undistorted* interstitial T or substitutional sites. Two types of approach have been used, with varying degree of sophistication. DeLeo *et al.*[28,29] used the self-consistent scattered-wave $X\alpha$ method in a small cluster to calculate the trends in the gap-level positions for several interstitial TM's. Hemstreet *et al.*[30,31] applied the same technique to substitutional TM's.

Zunger and Lindefelt[32–34] avoided the cluster size and surface problems by using a perturbative approach. They began with a perfect-crystal Green's function, then added the TM impurity as a localized perturbative potential (for a review, see Ref. 35). Beeler *et al.*[36,37] performed spin-unrestricted, self-consistent, linear muffin-tin orbital Green's-function calculations for all the $3d$ TM's at interstitial and substitutional sites. In addition to trends in the gap-level positions, they find that the early and late TM's in Si have a low spin. Finally, Lindefelt[38] estimated the magnitude of the relaxations around substitutional copper using an empirical valence-force potential, and found a symmetric outward relaxation of the nearest neighbors (NN's) by 0.24 Å.

The aim of the present paper is quite different. The positions of gap levels obtained at the *ab initio* HF level are well known to be only qualitative, and no attempt is made here at predicting the position of DLTS levels. Further, only copper is discussed. However, these are *ab initio* total-energy quantum-chemical calculations. Geometry optimizations are performed with no symmetry assumptions for a range of defect centers involving copper. The configurations, electronic structures, binding energies, and chemistry of these defects are obtained.

The methodology is discussed in Sec. II. Section III deals with interstitial and substitutional Cu, and Sec. IV discusses Cu-acceptor pairs. In Sec. V, the ring hexavacancy[39,40] is used as a model defect to study the interactions between several $Cu_i^+$'s and a nanometer-size void in the crystal. Section VI contains a discussion and conclusions.

## II. METHODOLOGY

The calculations were carried out at two complementary levels of theory. First, the geometries of the various complexes were gradient optimized with no symmetry assumptions using the ''approximate *ab initio*'' HF method of partial retention of diatomic differential overlap (PRDDO).[41,42] This method contains no experimentally adjusted parameters (hence ''*ab initio*'') but calculates only $\sim N^3$ two-electron integrals (hence, ''approximate''). In true *ab initio* HF calculations, $\sim N^4$ two-electron integrals must be evaluated, where $N$ is the basis set size. The reduction from $N^4$ to $N^3$ is accomplished by clever orthogonalizations of the basis set that render four-center integrals vanishingly small. The bottom line is that PRDDO reproduces the results of minimal basis set *ab initio* HF calculations at a fraction of the cost. It provides excellent geometries, but only approximate energetics and electronic structures. Note that optimizing the geometries of all the defects studied here at the *ab initio* HF level would be computationally prohibitive. For example, the $\{Cu_5,V_6\}$ complex involves 57 degrees of freedom!

The calculations were carried out in four H-saturated clusters[43] containing 22, 38, 44, and 100 Si atoms, respectively. The geometries optimized in the 38 and 44 host-atom clusters were used as inputs for single-point *ab initio* HF (Ref. 44) calculations with split-valence basis sets and polarization functions on selected atoms. A few geometries were reoptimized at the *ab initio* HF level, with some symmetry restrictions, in order to verify the PRDDO results (no discrepancies were found). In order to remove the core electrons from the calculations, Hay-Wadt pseudopotentials[45] for Si (and Al) and Stevens-Bash-Krauss pseudopotentials[46] for Cu (and Ga) were used. These pseudopotentials were successfully used in earlier calculations.[7]

In addition to equilibrium geometries and binding energies, these calculations provide energy eigenvalues, bond orders or degrees of bonding, overlap populations, and other parameters.[47] Mulliken charges allow one to compare the amount of charge *localized* on each atom. The population of the various (atomic) orbitals provides valuable information about the electronic configuration of the impurity. As noted above, the energy eigenvalues are not quantitative since the method does not optimize unoccupied states. The ''conduction band'' is unrealistically high in energy. However, the energy eigenvalues that are isolated in the gap are always associated with localized states. These eigenvalues provide information on the presence or absence of deep states associated with a given defect. The results reported below were obtained at the *ab initio* HF level except for the Cu-acceptor charge distributions in the 100 Si-atom cluster, which are PRDDO results.

## III. INTERSTITIAL AND SUBSTITUTIONAL COPPER

The present calculations confirm the earlier result[7] that the lowest-energy configuration of $Cu_i^+$ in Si is at (or rather, very near) the T site. The activation energy for diffusion[7] along the T-H-T path is 0.24 eV, very close to the most recent experimental value,[6] $0.18\pm0.01$ eV. The four nearest-neighbors (NN's) to $Cu_i^+$ relax outward by less than 0.05 Å. The energy spectrum of $Cu_i^+$ shows no localized state in the gap.

It *costs* 1.67 eV to insert the free $Cu^+$ ion into the T site in Si. This value is very close to the experimentally determined activation energy of solubility of copper, 1.7 eV.[1,18] Note that the experimental value is a heat of solution from a copper silicide, while the calculated energy difference is relative to the free $Cu^+$ ion. The agreement between the two numbers should therefore not be overinterpreted.

The electronic configuration of $Cu_i^+$ is *not* $3d^{10}4sp^0$ as is commonly assumed. This configuration is that of the free ion, but as an interstitial impurity in Si, copper promotes several electrons from the $3d$ into the $4sp$ shell and borrows some electron density from its NN's. This occurs even if the self-consistent cycle begins with a $3d^{10}$ guess orbital occu-

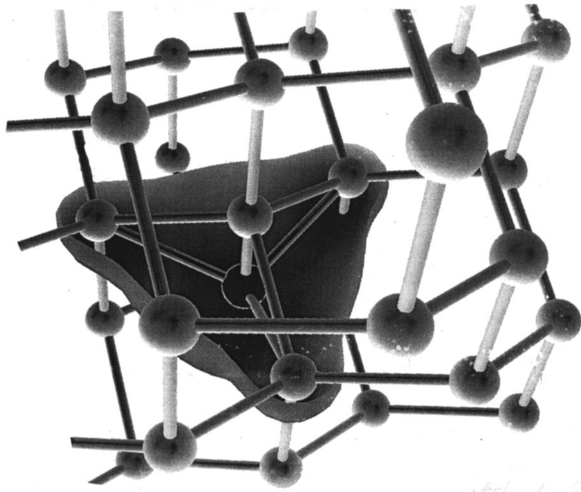


FIG. 1. Cross section of the electrostatic potential around $Cu_i^+$ (at the center of the surface, in black). The plot shows that the electrostatic potential around copper extends to cover its four NN's and that $Cu_i^+$ is not a spherical $3d^{10}4sp^0$ ball but promotes electrons to the $4sp$ shell in order to overlap with its four NN's.

pancy. $Cu_i^+$ *does not* resemble a tiny hard sphere, but overlaps (weakly but covalently) with its four NN's, as shown in Fig. 1.

The promotion of some electrons from the $3d$ to the $4sp$ shells allows some weak but covalent overlap with the crystal. The $3d$ orbital with the largest population is $3d_{xy}$, that is the orbital perpendicular to the T-H-T axis. The population of each of the four $4sp$ orbitals is about 0.9, a bit more in the $4p_z$ orbital along the trigonal axis. This small excess population pulls $Cu_i^+$ just off the T site toward the nearest Si atom on the trigonal axis. Since the bonding orbitals of the Si atoms point away from the impurity, the overlap between $Cu_i^+$ and its four NN's is very weak, but it is covalent: the overlap population is positive. The need to promote some electrons from the $3d$ orbitals to the $4sp$ ones—thus allowing some covalent overlap to occur—is much of the reason why it costs energy to insert copper into the crystal. Since copper has partially occupied $3d$ and $4sp$ shells, it is able to interact covalently with many impurities and defects, and can hybridize in a variety of ways. This is illustrated in the rest of this manuscript.

The Mulliken charge on $Cu_i^+$ is not $+1$, but close to zero. The $+1$ charge is delocalized further away from the interstitial. Note that if $Cu_i^+$ were the $3d^{10}4sp^0$ ion, its ionic radius[48] would be less than 0.75 Å, its Mulliken charge exactly $+1$, and its electrostatic potential would not look anything like that in Fig. 1. Since cluster or supercell calculations artificially localize any excess charge, they are inadequate to predict exactly how large a sphere around $Cu_i^+$ must be drawn to contain a net charge of $+1$. However, an examination of the changes in the charge distribution with and without $Cu_i^+$ in the 100-Si atom cluster shows that the $+1$ charge is localized within a sphere of radius *larger than* 10 Å. This result is consistent with the shallow donor behavior[24] assumed for interstitial copper. $Cu_i^+$ is not the point charge it is often thought to be.

When $Cu_i^+$ and a (neutral) vacancy get close to each other, copper becomes substitutional $Cu_s^+$, the only charge state of substitutional copper considered here. The energy spectrum shows the presence of several unoccupied energy levels in the gap. Their number and position are basis-set dependent, but their presence is not. The Koopman theorem ionization energy for this defect is negative, implying that it is an electron trap: adding one (or more) electron(s) occurs at a gain in energy. Substitutional copper is four-fold coordinated and overlaps covalently with its four NN's. None of these Cu–Si bonds are true two-electron covalent bonds. The bond orders are small and the bonds weak. The defect is very close to, but not exactly, tetrahedral: Of the nine valence orbitals associated with copper, the ones that have the largest population are $3d_{zz}$, $3d_{xy}$, and $4p_z$. The four NN's to copper relax outward by less than 0.1 Å.

The energy gained in the reaction $Cu_i^+ + V \rightarrow Cu_s^+$ is 2.71 eV (which does not include the formation energy of the vacancy). This is not a very large energy gain for a reaction involving an interstitial impurity and a vacancy. It corresponds to about 0.6 eV for each Cu–Si bond (some energy gain is associated with the reduction of the strain associated with the vacancy). For comparison, ones gains more than 3 eV by inserting a single H atom into a vacancy (which can accomodate four of them!) (Ref. 49) or a cluster of vacancies,[50] and the vacancy–self-interstitial recombination releases 8.2 eV.[51] It is possible that a single H interstitial could expel copper from its substitutional site, and two H's certainly would. Since the standard preparation of Schottky diodes results in some H penetrating into the subsurface layer,[52] this could explain why it is difficult to detect substitutional copper by DLTS.

## IV. COPPER-ACCEPTOR PAIRS

At low temperatures, copper removes[2,3,10] the electrical activity of shallow acceptors (in this paper, $A$ stands for B, Al, or Ga). The long-range attraction between $A^-$ and $Cu_i^+$ is Coulombic. Here, ''long-range'' means within a capture radius $R_c$ estimated[2] at 50 Å or so. However, the copper-acceptor dissociation energies reported in TID experiments are small and acceptor dependent, suggesting that the local interactions are not purely Coulombic. The dissociation energies[2] are 0.61, 0.70, and 0.71 eV for {Cu,B}, {Cu,Al}, and {Cu,Ga}, respectively.

An earlier study at a similar level of theory[26] showed that a weak covalent bond forms between Cu and B, with copper at the antibonding ($AB$) site of the acceptor. Thus, the nearby interaction implies passivation rather than compensation. Preliminary results from the present work[27] have shown that, were the interaction purely Coulombic, the dissociation energies should be substantially larger than reported in TID experiments. But the calculated *trends* were identical (and rather close) to the experimental ones: {Cu,Ga} is more stable than {Cu,Al} (by 0.08 eV), which itself is more stable than {Cu,B} (by 0.19 eV). The numbers in parentheses are total energy differences for the fully dissociated ions. Further, the dissociation energy $\{Cu,B\} \rightarrow Cu_i + B$ with copper at the second-nearest T site from B was found to be 0.69 eV, a value very close to the experimental one.

The present calculations involve three acceptors (B, Al, and Ga) and a combination of *ab initio* calculations in 44

Si-atom clusters and PRDDO calculations in the 100 Si-atom clusters. The results are as follows.

Geometry optimizations for the isolated acceptors show that $A^-$ remains on center and that its four NN's are drawn inward by 0.17 Å (in the case of $B^-$) and pushed outward in the case of $Al^-$ and $Ga^-$ (by 0.06 Å and 0.04 Å, respectively). The direction and magnitude of these relaxations are consistent with the sum of tetrahedral radii,[53] which are 2.03 Å for Si–B, 2.35 Å for Si–Si, and 2.40 Å for both Si–Al and Si–Ga. The corresponding sums with copper are 2.08 Å for Cu–B, 2.40 Å for Cu–Si, 2.46 Å for Cu–Al, and 2.45 Å for Cu-Ga.

The lowest-energy configuration with $Cu_i^+$ and $A^-$ in the same cluster occurs when copper is at the $AB$ site of the acceptor. In the optimized configurations, the internuclear distances are 1.98 Å for Cu–B, 2.15 Å for Cu–Al, and 1.98 Å for Cu–Ga. There is some overlap between copper and the acceptor. It is bonding in the case of B and Al, but antibonding in the case of Ga. The largest changes in the Cu orbital populations relative to isolated $Cu_i^+$ occur in the $3d_{xy}$ and $4p_z$ orbitals, where $z$ is the copper-acceptor axis. When the interaction is bonding, the population in $3d_{xy}$ decreases and that in $4p_z$ increases. When the interaction is antibonding, it is the $3d_{xy}$ orbital that increases its population at the expense of the $4p_z$, and the charge density on Cu looks a little more like a doughnut perpendicular to the trigonal axis. In the case of $Cu_i^+$, the population in $3d_{xy}$ is 1.21. This changes to 0.77, 0.91, and 1.35 for {Cu,B}, {Cu,Al}, and {Cu,Ga}, respectively.

All the T sites in the cluster (other than the one immediately next to the $AB$ site of the acceptor) are local minima of the potential energy for interstitial copper. The energy for Cu at these sites is higher than that of the {Cu,A} pair by several tenths of an eV. For example, the $A$–Si–Cu configuration (Cu antibonding to a host atom instead of the acceptor), is higher by 0.55, 0.58, and 0.57 eV for B, Al, and Ga, respectively. Along the most likely dissociation path, if one pulls Cu away from the $AB$ site through the H site to the next T site on the same ⟨111⟩ axis, the energy goes up by 0.45 eV in the case of B. If one adds to that the 0.24 eV barrier at the H site, the calculated {Cu,B} dissociation energy becomes 0.69 eV, surprisingly close to the experimental value (0.61 eV). The energy difference is 0.88 eV for {Cu,Al} and 0.92 eV for {Cu,Ga} (experimentally, 0.70 and 0.71 eV, respectively). These calculated values imply that most of the measured dissociation energy in the TID experiments[2,10] corresponds to the break up of the pair. Yet, these experiments drive copper far away from the acceptor, as if there were no need to overcome a long-range Coulomb attraction between the two species.

An analysis of the changes in the Mulliken charges on Cu and the acceptor in the same cluster shows that copper compensates the acceptor even at rather large separations. This implies a charge transfer $A^- + Cu^+ \rightarrow A^0 + Cu^0$ within some volume around the acceptor. These calculations were performed in the $CuASi_{99}H_{72}$ cluster in which the two impurities can be placed at local minima of the energy as far as 10.4 Å apart, both impurities still having two complete host atoms shells around them. Three configurations were considered and the Mulliken charges compared. In each case, the change in the charge on the copper and the acceptor atoms is very small. For example, in the case of Cu and Al, the passivated configuration has $+0.01e$ on Cu and $+0.15e$ on Al. If Cu is at a T site 4.4 Å away from Al, the charge on Cu is unchanged and that on Al drops to $+0.07e$. When Cu is at a T site 10.4 Å away from Al, it still has the same Mulliken charge, while that on Al drops further to $+0.05e$. Thus, even when copper and the acceptor are over 10 Å apart, they do not behave like $+1$ and $-1$ point charges. Similar trends occur in the cases of B and Ga. As noted above, the charge on $Cu_i^+$ spreads out over many NN's, and so does that of $A^-$. When $Cu_i^+$ is in the neighborhood of the acceptor, the two charge clouds overlap and substantially cancel each other. There is no immediate charge transfer $\{A,Cu\} \rightarrow A^- + Cu^+$ when the Cu–$A$ bond breaks.

Thus, while copper *passivates* the acceptor in the lowest-energy configuration, it *compensates* it for separations at least as large as 10.4 Å. Assuming a Coulomb potential at short distances is therefore incorrect. The dissociation of the copper-acceptor pair does not reactivate the acceptor until the two species are at a substantial separation, where an already heavily screened Coulomb interaction kicks in.

## V. COPPER PRECIPITATION AT INTERNAL VOIDS

The model intrinsic defect considered in the present study is the ring-hexavacancy ($V_6$), which is predicted[39,40] to be extremely stable and electrically inactive. This defect consists of an entire hexagonal ring missing from the crystal. It is an ellipsoidal void of diameter 7.8 Å and thickness 4.4 Å. It has trigonal symmetry, with 12 Si NN's around the ⟨111⟩ axis and two Si NN's on the trigonal axis, which also participate in the reconstruction. These 14 host atoms must be included in all the geometry optimizations, in addition to any impurities inside $V_6$. There are two issues to consider when calculating the precipitation of $Cu_i^+$.

First, the defect cannot build up too much charge. If one assumes that several $Cu_i^+$'s precipitate and no electron is ever trapped, the defect rapidly builds up excessive positive charge and becomes a long-range repulsive center for additional $Cu_i^+$'s. This was proposed[54] as the reason why copper precipitates much easier in *n*-type than in *p*-type Si. However, since copper precipitates are also observed in *p*-type material, electrons must trap at the defect to maintain a small or zero net charge. Such a charge neutralization process is assumed here.

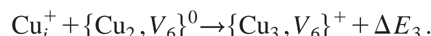
Second, only total energy differences of *closed-shell* (spin 0) configurations are directly comparable. In principle, restricted open-shell calculations (ROHF) for the spin-$\frac{1}{2}$ configurations could be carried out and would produce energies that are comparable to the closed-shell (RHF) ones. However, optimizing geometries at the ROHF level for the complexes studied here is far too computer intensive, especially since PRDDO is ill equipped to perform such calculations. Therefore, total energy differences involving only closed-shell configurations are included below. The precipitation of $Cu_i^+$ at $V_6$ was handled as follows.

(1) $Cu^+$ is placed inside $V_6$, the geometry optimized, and the energy gain $\Delta E_1$ relative to $Cu_i^+$ is defined as

$$Cu_i^+ + V_6 \rightarrow \{Cu_1, V_6\}^+ + \Delta E_1 .$$

The calculated gain is $\Delta E_1=3.36$ eV. It is then assumed that $\{Cu_1,V_6\}^+$ captures an electron, then traps $Cu_i^+$. This defect traps a second electron and the geometry of $\{Cu_2,V_6\}^0$ is optimized. This defect, a closed shell, is the next trap for $Cu_i^+$.

(2) $Cu^+$ is placed inside $\{Cu_2,V_6\}^0$, the geometry optimized, and the energy gain $\Delta E_3$ relative to $Cu_i^+$ is defined as



$$Cu_i^+ + \{Cu_2,V_6\}^0 \rightarrow \{Cu_3,V_6\}^+ + \Delta E_3.$$

The calculated gain is $\Delta E_3=4.94$ eV. It is then assumed that $\{Cu_3,V_6\}^+$ captures an electron, then traps $Cu_i^+$. This defect traps a second electron and the geometry of $\{Cu_4,V_6\}^0$ is optimized. This defect, a closed shell, is the next trap for $Cu_i^+$.

(3) $Cu^+$ is placed inside $\{Cu_4,V_6\}^0$, the geometry optimized, and the energy gain $\Delta E_5$ relative to $Cu_i^+$ is defined as

$$Cu_i^+ + \{Cu_4,V_6\}^0 \rightarrow \{Cu_5,V_6\}^+ + \Delta E_5 \text{ eV}.$$

The calculated gain is $\Delta E_5=2.01$ eV.

The process could continue for a larger void, but the hexavacancy is filling up. This complex may grow, for example involving sites for Cu outside $V_6$. This possibility is not considered here.

The geometrical configurations of $\{Cu_n,V_6\}^0$ and $\{Cu_n,V_6\}^+$ are very similar to each other. The electron removed from the neutral complex comes from a molecular orbital rather delocalized around $V_6$ and does not affect the geometry much at all. The optimized configurations of the $\{Cu_n,V_6\}$ complexes with $n=0,\ldots,5$ are shown in Fig. 2. In $V_6$, copper cannot be described as simply ''interstitial'' or ''substitutional.'' Instead, the geometry of all the 14 Si atoms and $n$ Cu atoms must always be reoptimized in order to find the lowest-energy configuration.

A careful analysis of the orbital populations of the Cu impurities trapped in $V_6$ reveals that the copper atoms bind to the inner surface of the void using the nine valence orbitals at their disposal. No two Cu's are identically hybridized in the void. Yet several remarkable trends are worth noticing.

(1) In a void, the Cu impurities remain *as far apart as possible* from each other. In $\{Cu_2,V_6\}$, the two Cu's are at opposite inner surfaces. In $\{Cu_3,V_6\}$, the three Cu's form an isosceles triangle. In $\{Cu_4,V_6\}$, the four Cu's form a rectangle in the plane of $V_6$, amd $\{Cu_5, V_6\}$ is a pyramid, the tip of which is on the trigonal axis.

(2) *Cu–Si covalent overlap* is preferred over Cu–Cu overlap. This is consistent with the bond strengths in diatomics[48] (2.3 eV for Cu–Si vs 1.8 eV for Cu–Cu). As long as there is plenty of room in the void, the Cu's bind to different Si atoms. As the void fills up, some Cu–Cu overlap becomes unavoidable, and a few Si atoms bind to two Cu atoms.

(3) Each Cu forms weak covalent bonds to *precisely four* Si atoms. This observation is not simply based on a compilation of Cu–Si internuclear distances, but on the requirement that, for a given {Cu,Si} pair, the degree of bonding be non-negligible and the overlap population positive (that is, a bonding overlap). The ''degree of bonding''[55] is a measure of the amount of covalent overlap between two atoms. It is not proportional to the bond strength but is defined in such a way that it is 2.0 for a 4-electron covalent bond (e.g., $O_2$), 1.0 for a two-electron covalent bond (e.g., $H_2$), and 0.0 if the bond is purely ionic (e.g., NaCl). In the case of the $\{Cu_n,V_6\}$ complexes, the degrees of bonding involving copper are all in the 0.4 to 0.8 range, that is Cu always forms several weak bonds, and even the strongest ones are quite a bit less than a true two-electron bond (degree of bonding 1.0).

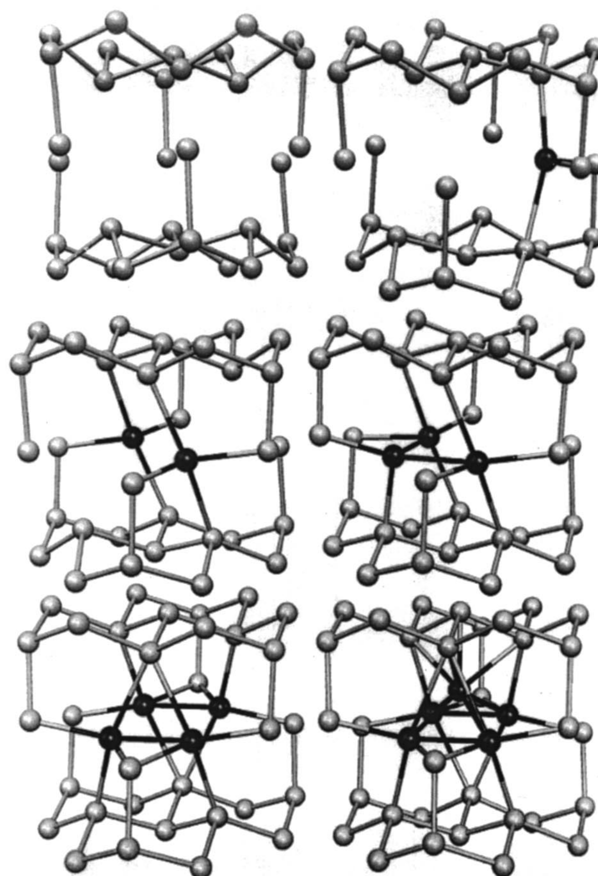


FIG. 2. Energy-optimized configurations of the $\{Cu_n,V_6\}$ complexes for $n=0,\ldots,5$, from top to bottom and left to right. The copper atoms are in black (see text).

(4) The sum of the degrees of bonding associated with each Cu in any of the $\{Cu_n,V_6\}$ complexes varies only in the *narrow range 2.3 to 2.6*. Thus, the total number of electrons participating in the covalent bonding of Cu to an internal void is *always around five*. These electrons are distributed among four Cu–Si bonds (plus any Cu–Cu bonds).

(5) The maximum strength of each of the Cu–Si bonds is 0.9 eV (that is, less than the width of the gap). This estimate is obtained by dividing the binding energy of Cu to $\{Cu_n,V_6\}$ (relative to $Cu_i^+$) by the number of Cu–Si bonds involved. Since each copper forms four inequivalent Cu–Si bonds with degrees of bonding ranging from 0.4 to 0.8, some of the bonds are necessarily weaker than 0.9 eV. This has the following two consequences.

(5a) At least some of the energy eigenvalues associated with the bonding/antibonding orbitals of the weak Cu–Si (and Cu–Cu) bonds are in the gap. In the HF calculations, many energy eigenvalues are clearly visible in the gap of the energy spectrum for all the $\{Cu_n,V_6\}$ complexes. The localized (deep) levels are associated with the Cu-Si bond. This shows that the electrical activity of copper precipitates in internal voids is associated with the weak Cu–Si bonds. This

is consistent with the interpretation[56,57] that the electrical activity of copper precipitates originates at the interface between Si and the precipitates.

(5b) The binding energy of a single hydrogen to a vacancy[49] or vacancy aggregate[50] is of the order of 3 eV (this results from the formation of one strong Si–H bond). Thus, if interstitial hydrogen is present, it will easily displace Cu from internal voids, since replacing even the strongest Cu–Si bond by a Si–H bond results in a gain of the order of 2 eV. Such an effect has indeed been reported.[18]

A brief description of the configurations in Fig. 2 is as follows.

In $\{Cu_1, V_6\}$, copper binds to four Si atoms on the inner surface of the void. The four Cu–Si distances range from 2.38 to 2.68 Å, and the degrees of bonding from 0.6 to 0.4. The binding energy relative to $Cu_i^+$ is 3.36 eV.

In $\{Cu_2, V_6\}$, the two copper atoms are as far from each other as possible (4.55 Å), at opposite inner surfaces of $V_6$. The Cu–Si bond lengths vary from 2.38 to 2.62 Å, and the degrees of bonding from 0.7 to 0.5.

In $\{Cu_3, V_6\}$, the three copper atoms form an almost perfect isosceles triangle in the plane of $V_6$. The Cu–Cu distances are 2.75, 2.77, and 4.08 Å, respectively. One Cu is bound to the two other Cu's, but the overlap is very small (degree of bonding $\leq 0.2$ and overlap population $\sim 0.1$). This Cu is mostly bound to only two Si atoms, at 2.28 and 2.33 Å, with degrees of bonding of 0.7 and 0.8. The other two coppers form the usual four Cu–Si bonds, with bond lengths varying from 2.38 to 2.71 Å and degrees of bonding from 0.6 to 0.4. The binding energy of $Cu_i^+$ to this complex is the highest in the series, 4.9 eV. The reason why this value is so large is not clear at this point. However, it indicates a tendency for Cu to precipitate since, given a choice between trapping at $V_6$ or at $\{Cu_2, V_6\}$, copper would prefer the latter.

The copper atoms in $\{Cu_4, V_6\}$ form a perfect rectangle in the plane of $V_6$. The rectangle has width 2.36 Å and length 3.67 Å . There are two weak Cu–Cu bonds (degree of bonding 0.4), that is each of the four Cu's is bound to one Cu and four Si atoms. These bonds are similar to those described above.

Finally, $\{Cu_5, V_6\}$ is a slightly distorted version of $\{Cu_4, V_6\}$, with the fifth Cu forming the tip of a pyramid with a rectangular base, the tip being on the trigonal axis of $V_6$. The fifth Cu is eightfold coordinated but the degrees of bonding vary only from 0.2 to 0.4. The other coppers are roughly as described above for $\{Cu_4, V_6\}$. The binding energy relative to $\{Cu_4, V_6\}$ and $Cu_i^+$ is 2.01 eV.

Note that this value is consistent with the measured[18] dissociation energy of copper from internal voids, 2.2±0.2 eV. However, our results show that some of the Cu's trapped in a void are more strongly bound than others.

## VI. SUMMARY AND CONCLUSIONS

Interstitial copper and its interactions with a vacancy, shallow acceptors, and an internal void are studied at the *ab initio* HF level in clusters ranging in size from 22 to 100 Si atoms. The geometries of the various defects are gradient optimized at the approximate *ab initio* level (PRDDO) and the optimized geometries used as inputs for single-point *ab initio* HF calculations with split-valence basis sets and polarization functions on selected atoms.

The $Cu_i^+$ ion is at (or very near) the T site. It is not in the chemically inert $3d^{10}4sp^0$ configuration. Instead, almost four electrons are promoted from the $3d$ into the $4sp$ shell. This allows copper to form weak but covalent bonds to a wide range of impurities and defects. Even the isolated interstitial ion shows some covalent overlap with its four Si NN's.

The activation energy for diffusion[7] of $Cu_i^+$ along the T–H–T path is 0.24 eV, very close to the most recent experimental[6] value, 0.18± 0.01 eV. It costs 1.67 eV to insert the free copper ion into the T site in Si. This value coincides with the experimentally determined heat of solution from a copper silicide (1.7 eV).[1,18]

Substitutional copper, $Cu_s^+$, is fourfold coordinated. Its binding energy (relative to $Cu_i^+$) is 2.7 eV. It is an electron trap. $Cu_s^0$ and $Cu_s^-$ are not considered here.

The lowest-energy configuration for interstitial copper in the same cluster as a B, Al, or Ga acceptor is at the *AB* site of the acceptor. The overlap between Cu and the acceptor is weakly bonding in the case of B and Al, and weakly antibonding in the case of Ga. The energy required to separate the copper-acceptor pairs by bringing Cu over the H site (to the second-nearest T site from the acceptor) is 0.69, 0.88, and 0.92 eV in the case of B, Al, and Ga, respectively. These values compare well with the dissociation energies measured by TID, 0.61, 0.70, and 0.71 eV, respectively.

Since the copper-acceptor binding energies are within a tenth of an eV or so of each other, it is difficult to pinpoint the reason why the {Cu,B} pair is the weakest of the copper-acceptor pairs. The most obvious reason is that the lattice relaxation around boron is the largest: $B^-$ substantially pulls its NN's toward it, while $Al^-$ and $Ga^-$ leave the crystal virtually unchanged. This affects the local environment around copper, which cannot optimize both the Cu–Si and Cu–B distances. The sum of the tetrahedral radii is in the range 2.35 to 2.45 Å for Si–Si, Si–Al, Si–Ga, Cu–Si, Cu–B, Cu–Al, and Cu–Ga, but it is only 2.03 Å for Si–B.

Once the $\{Cu, A\}$ pair is broken, the Mulliken charge on both Cu and the acceptor remain virtually unchanged for separations of *at least* 10.4 Å (the maximum possible in the largest cluster used here). This implies that while copper *passivates* the acceptor in the lowest-energy configuration, the two species *compensate* each other up to a fairly large separation. The screened Coulomb attraction between $Cu_i^+$ and $A^-$ kicks in only farther out.

The binding energies of $Cu_i^+$ to a monovacancy and a hexavacancy are summarized in Fig. 3. Note that vacancy clusters are used here to model internal voids. However, they are believed to form in the core of dislocations[15,58] as well, where they become plausible gettering sites for impurities such as TM's. Copper shows a strong tendency to precipitate at internal voids such as $V_6$. All the copper impurities in all the precipitates studied here show a very similar behavior.

(1) The Cu's stick to the inner surface of the void and remain as far away from each other as possible. (2) Cu–Si bonding is preferred over Cu–Cu bonding. (3) Each Cu binds to four Si atoms. (4) A total of about five electrons participate in the bonding of each Cu (this includes the electrons associated with the Cu and Si atoms). (5) Each of the

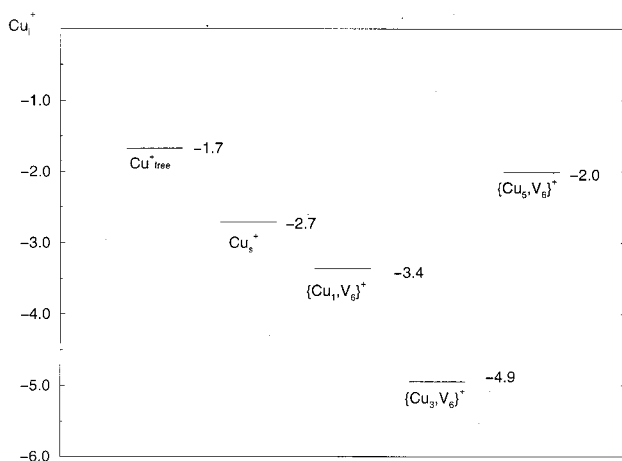



FIG. 3. Energy of $Cu^+_{free}$ (a), $Cu_s^+$ (b), $\{Cu_1,V_6\}^+$ (c), $\{Cu_3,V_6\}^+$ (d), and $\{Cu_5,V_6\}^+$ (f), all relative to $Cu_i^+$.

Cu–Si bonds is substantially weaker than a two-electron covalent bond. (6) At least some of the bonding/antibonding energy levels associated with the weak Cu–Si (and Cu–Cu) bonds are in the gap, strongly suggesting that they are responsible for the electrical activity of Cu precipitates. (7) Since the binding energy of one H to a cavity such as $V_6$ is about 3 eV per Si–H bond, H will easily displace Cu from such precipitates, as observed.[18] (8) Finally, the binding energies of $\{Cu_n,V_6\}^+$ relative to $\{Cu_{n-1},V_6\}^0+Cu_i^+$ vary with $n$. For $n=1$, it is 3.36 eV. For $n=3$, it is 4.94 eV. For $n=5$, it drops to 2.01 eV. The latter value, which corresponds to $V_6$ saturated with Cu's, matches the experimental value[18] for the binding energy of Cu at internal voids, 2.2 $\pm$0.2 eV relative to the solution in Si.

This paper did not address the interactions between $Cu_i^+$'s and divacancies, but the hexavacancy results suggest that one or more Cu's will trap in $\{V_2\}$, bind to its inner surface, and change its electrical and optical properties. There is no reason to suspect that the chemistry of copper in a divacancy is qualitatively different from that in the defects considered here. The ''passivation'' of divacancies by Cu suggested in Ref. 14 is probably a substantial change in the electrical properties of the complex, making it look different, rather than a passivation in the usual sense (no more electrically active levels in the gap).

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