Copper interactions with H, O, and the self-interstitial in silicon

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The interactions between *substitutional* copper in Si and one to four hydrogen interstitials are studied using first-principles molecular-dynamics simulations. Up to three H's can bind covalently to one Cu_s. These complexes have been observed by deep level transient spectroscopy. The structures and binding energies are calculated, and the vibrational modes predicted. Although $\{Cu_s, H_4\}$ does have a small binding energy relative to $\{Cu_s, H_3\} + H_{BC}$, constant-temperature dynamics show that this complex is not stable. It can break up in several ways, one of them is the dissociation into $Cu_s + 2H_2$ molecules. The interactions between interstitial copper and interstitial oxygen show that Cu_i^+ prefers to be in the slightly larger void adjacent to O_i, but the binding energy is quite small (0.31 eV) and no covalent Cu-O overlap occurs. The interactions of Cu_i with an *A* center (oxygen-vacancy complex) involve a kickout $Cu_i + \{O, V\} \rightarrow \{Cu_s, O_i\} + 1.7$ eV, with O_i bridging a Si-Si bond immediately adjacent to Cu, which itself is at a slightly perturbed substitutional site. Again, no covalent Cu-O bonding occurs. Finally, Cu_i interacts with the self-interstitial by pushing it and one host atom away from a perfect substitutional site and moving itself toward it, at a gain of 1.6 eV.

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I. INTRODUCTION

Copper is of special interest among the $3d$ transition metal (TM) impurities,[1,2] because it is used for interconnects on computer chips. It also easily contaminates bulk Si during processes such as the chemomechanical polishing of wafers. In p-type and intrinsic Si, most of the copper exists as the interstitial Cu_i^+ ion, with its lowest energy at the tetrahedral interstitial (T) site. It is one of the fastest-diffusing impurities in Si, with a migration energy predicted[3] to be less than 0.24 eV and measured[4] at 0.18 ± 0.02 eV. The solubility of copper in Si is low, and it tends to precipitate at/near vacancy like defects, stacking faults, grain boundaries, oxygen precipitates, or out diffuse to the surface of the sample.[1,2,5–8] Most copper complexes and precipitates are electrically and optically active, apparently impossible to passivate, and little microscopic information about their structure and chemistry is available. However, the substitutional-interstitial $\{Cu_s, Cu_i\}$ pair has been studied by deep-level transient spectroscopy (DLTS), photoluminescence (PL) and first-principles theory.[9–12] Furthermore, several $\{Cu_s, H_n\}$ complexes have been seen by DLTS.

The first experimental studies of TM-H complexes were done in Ge (Refs. 14–16) by photothermal ionization spectroscopy, and the authors reported that hydrogen affects the electrical activity of the TM. The ability of hydrogen[13] to passivate the electrical activity of a range of impurities and defects in Si provided the impetus for the study of TM-H complexes in Si as well. Numerous such complexes have now been observed but few are passivated. Following hydrogenation by wet chemical etching, the shifts of the electrical levels of many substitutional TM impurity have been monitored by DLTS, Laplace-DLTS, or thermally stimulated capacitance. In some cases, deep-level depth profiling was used to demonstrate how many H's are trapped at a given TM. The general rule is that complexes such as $\{TM, H_1\}$, $\{TM, H_2\}$, and sometimes even $\{TM, H_3\}$ are still electrically active, but the TM's gap levels shift within the gap. This behavior was observed for Ti,[17,18] V,[17,19,20] Fe,[21–25] Cr,[17,19] Co,[26] Ni,[25,27] Cu,[28–31] Rh,[32] Pd,[33] Ag,[21,34] Pt,[35–37] and Au.[17,38–42] The trends and assignments of the many DLTS peaks have been discussed.[43,44] In the case of Pt (Refs. 45–48) and Au (Refs. 49–51), additional information about their microscopic structure has been obtained by electron paramagnetic resonance (EPR) and Fourier transform infrared absorption (FTIR) spectroscopy. Several first-principles theoretical studies of $\{TM, H_n\}$ complexes have been performed for Ni,[52] Pd,[53] Ag,[53,54] Pt,[53,55] and Au.[53–55] The authors have concluded that in all cases, H traps at the antibonding (AB) site of a Si host atom adjacent to the substitutional TM.

Despite the apparent similarities in the predicted and observed behavior of the $\{TM, H_n\}$ complexes, the evidence is insufficient to conclude that all these complexes have identical geometrical configurations $TM \cdots Si\text{-}H_{AB}$. For example, the FTIR spectra of the $\{Pt, D\}$ complex fail to show[56] the ^{29}Si and ^{30}Si isotope shifts that would be expected were D bound to a Si adjacent to Pt. Further, the annealing temperatures of the various $\{TM, H_n\}$ complexes vary much more than might be expected if one always dealt with (almost) the same Si-H_{AB} bond. Finally, our preliminary calculations[10] concluded that in the case of $\{Cu_s, H_n\}$ complexes, H binds directly to the TM and not to a nearby Si atom. This implies that the chemical nature of the TM itself plays an important role. Therefore, we refrain from generalizations and focus on the microscopic properties of Cu and its complexes in Si without implying that our predictions can or should be extended to TM's other than Cu.

Copper in Si exists predominantly as the Cu_i^+ interstitial, a species that was found to have no affinity for hydrogen.[3]

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Further, hydrogen was shown[57] to displace copper trapped in internal voids, suggesting that no {Cu,H} complexes form under these conditions either. However, when Cu is introduced into the material at high temperatures, a fraction of it traps at vacancies and forms the stable Cu_s defect. Theory predicts that the $Cu_i + V \rightarrow Cu_s$ releases 2.5 to 2.8 eV,[10,58] values which *exclude* the formation energy of the vacancy [4 eV (Ref. 59)]. The vacancy must be provided to Cu_i in order to form Cu_s. The vacancies are available at high temperatures during the in-diffusion of copper. Three electrical levels associated with Cu_s have been identified:[60,61] $\{0/+\}$ at $E_v + 0.20$ eV, $\{-/0\}$ at $E_v + 0.41$ eV, and $\{--/-\}$ at $E_c - 0.17$ eV.

Cu_s traps Cu_i and forms the $\{Cu_s, Cu_i\}$ pair (for an overview of the experimental data and the most recent theoretical study, see Ref. 12). Upon hydrogenation, Cu_s is observed by DLTS to trap up to three H interstitials and the electrical levels of these $\{Cu_s, H_n\}$ complexes have been identified.[9,30,31] Annealing studies show that these complexes are stable up to at least 100 °C. There is no FTIR spectrum of any of these complexes because they have been observed so far only in low concentrations in thin sub-surface layers following hydrogenation from a wet chemical etch.

Zundel and co-workers[62] were the first to notice a decrease in the diffusivity of copper in Czochralski silicon (CZ-Si) caused by a weak trap, the concentration of which matches that of interstitial oxygen O_i. Mesli *et al.*[63] (see also the review in Ref. 2) performed transient-ion-drift experiments in comparably doped (p-type) float zone and CZ Si. The O concentration in the former sample is about two orders of magnitude smaller than in the latter. They demonstrated the existence of a $\{Cu_i, O_i\}^+$ pair with the binding enthalpy 0.20 ± 0.05 eV.[63] Hage *et al.*[64] reported a rather broad O-related mode at 1038 cm^{-1} that appears following the introduction of Cu. However, this line has been seen only in samples with a high B concentration. The presence of metal impurities such as copper has an opposite influence on the diffusion of oxygen. Infrared studies[65] of the annealing of the dichroism of the oxygen absorption lines found an enhanced diffusion of oxygen when copper is introduced in the sample. Newman *et al.* explained this observation by an indirect mechanism involving no *direct* copper-oxygen interactions, using Woodbury and Ludwig's[66] proposal that the presence of Cu_i increases the vacancy concentration.

In this paper, we discuss the interactions between Cu_s and H, Cu_i and O_i, Cu_i and the {O,V} complex (A center), and Cu_i and a self-interstitial. The results include the formation dynamics, stable configurations, binding energies, and vibrational spectra.

II. THEORETICAL APPROACH

The results discussed below were obtained from self-consistent, first-principles molecular-dynamics (MD) simulations based on (spin-averaged and spin polarized) density-functional (DF) theory within the local density approximation. The calculations are performed with the SIESTA code.[67,68] The exchange-correlation potential is that of Ceperley-Alder[69] as parametrized by Perdew and Zunger.[70] Norm-conserving pseudopotentials in the Kleinman-Bylander form[71] are used to remove the core regions from the calculations. The Cu pseudopotential includes relativistic corrections. The basis sets for the valence states are linear combinations of numerical atomic orbitals of the Sankey type[72,73] but generalized to be arbitrarily complete with the inclusion of multiple-zeta orbitals and polarization states.[67] The charge density is projected on a real-space grid with an equivalent cutoff of 150 Ry to calculate the exchange-correlation and Hartree potentials. This large cutoff is needed to describe the localized d states of copper (tests up to 250 Ry confirm that it is sufficient).

The host crystal is represented by a 64-host atom periodic supercell in most calculations, but a few runs in a 128-cell were performed and confirm that the 64-cell is appropriate for all the defects studied here. Cell size effects have recently been considered in the case of copper pairs,[12] which are complexes of comparable size to the ones considered here. Only minor shifts in the calculated frequencies and very small (or no) changes in geometries have been observed.

The calculations used double-zeta (DZ) basis sets, with polarization functions (DZP) for Cu. The geometries were all optimized with a $2\times2\times2$ Monkhorst-Pack[74] mesh for k-point sampling as well as with $k=0$ (Γ point). As reported earlier,[75] total energy differences are affected by (typically) 0.2 eV. The energetics given below are the ones obtained with the $2\times2\times2$ mesh. The constant-temperature MD runs employed the Nosé thermostat.[76] Some were done with single-zeta (SZ) then a DZ basis sets to confirm the results. Constant-T simulations were all done with $k=0$ only. The time step was 0.2 fs with H in the cell, 1.5 fs with O in the cell, and 2.0 fs when only Si and Cu were present.

The local vibrational modes (LVM's) were calculated using the perturbative approach developed by Pruneda.[77] It allows the computation of the (harmonic) dynamical matrix. The matrix elements are extracted at $T=0$ K from the derivatives of the density matrix relative to nuclear coordinates. The density matrix must be as accurate as possible, which implies large basis sets. Further, the geometry of the system must be very well converged (maximum force smaller than 0.003 eV/Å). These calculations are limited to $k=0$ Recent predictions[77] of some 70 known LVM's in Si have shown that the calculated frequencies have an average error relative to experiment of the order of 2%.

III. INTERACTIONS OF Cu_s WITH H

Substitutional copper (Cu_s) forms whenever Cu_i encounters a preexisting vacancy. The reaction $Cu_i + V \rightarrow Cu_s$ releases 2.5 eV at the Hartree-Fock (HF) level[58] and 2.8 eV with SIESTA.[10,12] HF and DF calculations find that Cu_s is on-center, fourfold coordinated, and that virtually no lattice distortion occurs because the Cu-Cu, Cu-Si, and Si-Si bond lengths are within 0.1 Å or so of each other. The on-site location of Cu_s and its calculated binding energy are consistent with a (high-temperature) copper-related center observed by channeling.[78] HF and DF calculations predict that Cu in Si populates its $4sp$ shell at the expense of the $3d$ shell. While the exact number of electrons promoted varies with

the level of theory, both HF and DF theory predict that even Cu_i^+ in Si is *not* $3d^{10}$ but $3d^{10-x}4(sp)^x$, with $x \leq 1$. In the case of Cu_s, some $3d$ electrons do participate in the bonding. The four Cu-Si bonds are weak but covalent. Since virtually no lattice strain occurs around Cu_s, we estimate that the bond strength of each of the four Cu-Si bonds is of the order of 2.8 eV/4=0.7 eV.

We performed a number of constant-temperature MD simulations at $T = 1000$ K in cells containing Cu_s as well as one, two, three, or four H interstitials to investigate if and how H traps at or near Cu_s. Such an elevated temperature was chosen in order to probe the potential surface quickly (within a few thousand time steps). In all cases, H moves directly toward Cu_s without disturbing Si-Si or Cu-Si bonds: H binds to Cu_s along directions that are away from (but not antibonding to) Cu-Si bonds. In these simulations, the H's have too much kinetic energy to remain bound to Cu_s. They "bounce off" of it but keep on coming back in the same manner.

Geometry optimizations were done (conjugate gradients) to find all the local minima of the potential surface for one to four H interstitials at/near Cu_s. This includes bond-centered (BC) configurations ($Cu_s \cdots H \cdots Si$ or Cu_s-$Si \cdots H \cdots Si$), the antibonding (AB) site of a Si bound to Cu ($Cu_s \cdots Si$ -H_{AB}), and H bound directly to Cu_s with a range of Cu-H directions. When more than one H was involved, all the combinations of such structures were tested. Spin polarization does not affect the structures or energy differences.

The lowest-energy configurations all have Cu-H bonds with no Si-H overlap. Thus, $\{Cu_s, H_1\}$, $\{Cu_s, H_2\}$, and $\{Cu_s, H_3\}$ have copper fivefold , sixfold, and sevenfold coordinated, respectively (Figs. 1). The $\{Cu_s, H_4\}$ complex will be discussed below.

Metastable configurations (local minima of the potential energy) do exist at $T = 0$ K. We used a "heat treatment" to check their stability. Starting in the optimized metastable configuration, we raised the temperature of the cell to a few hundred degrees (typically 500–1000 K), allowed the system to evolve for about 1000 time steps, then quenched rapidly to see if the configuration had changed. In all cases, we found that a single configuration survives, the one discussed above. In particular, the configurations that have H at the AB site of a Si adjacent to Cu ($Cu_s \cdots Si$-H_{AB}) are unstable and do not survive the heat treatment.

Note that in almost all H-impurity complexes in Si,[13] hydrogen is bound to (or predominantly to) a host Si atom adjacent to the impurity, sometimes in a BC configuration, sometimes at an AB site. It is unusual for H to bind directly to the impurity in a manner that does not involve any Si participation. This is made possible in the case of TM's by their ability to achieve many more coordination numbers than elements with no d valence orbitals. As mentioned above, Cu_s uses some of its $3d$ electrons to form four Cu-Si bonds, and once the $3d$ shell is open, unusual hybridizations become possible.

The binding energies ΔE_n ($n = 1, \ldots, 4$) of the $\{Cu_s, H_n\}$ complexes were calculated relative to isolated neutral BC hydrogen

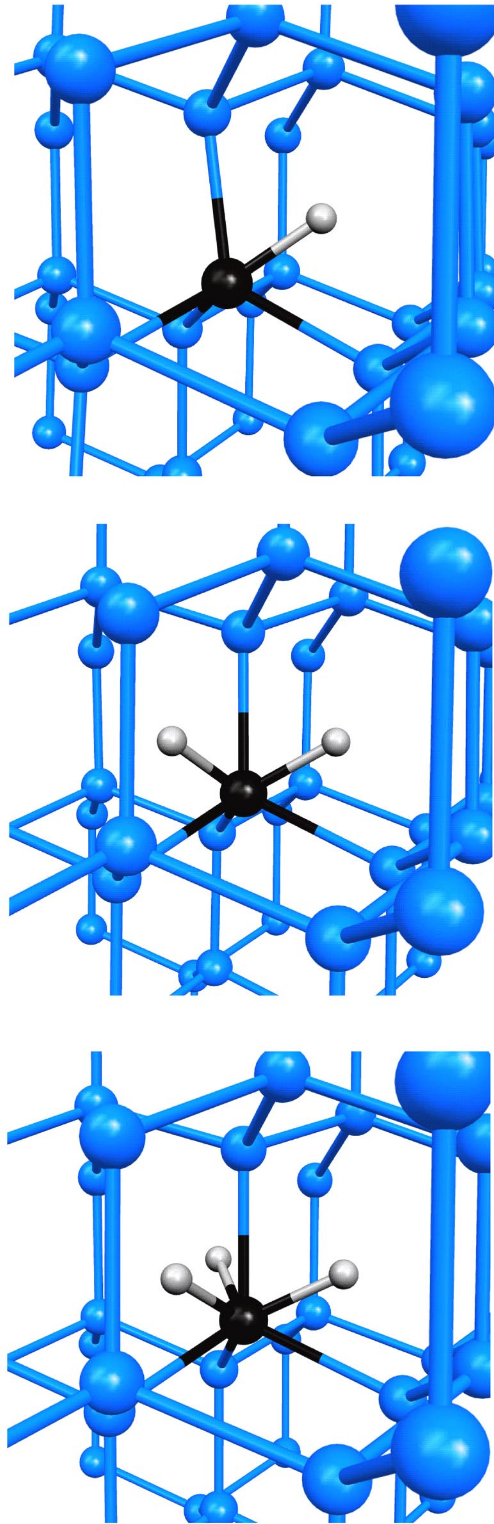

FIG. 1. (Color online) The $\{Cu_s, H_1\}$ (top), $\{Cu_s, H_2\}$ (middle), and $\{Cu_s, H_3\}$ (bottom) complexes in Si have H (small white sphere) bound directly to Cu (black sphere) with no H-Si overlap. Copper is fivefold, sixfold, and sevenfold coordinated, respectively.

$$\{\mathrm{Cu}_s,\mathrm{H}_{n-1}\}+\mathrm{H}_{\mathrm{BC}}\rightarrow\{Cu_s,\mathrm{H}_n\}+\Delta E_n .$$

The values obtained with a $2\times2\times2$ Monkhorst-Pack mesh are larger than the ones we reported earlier with only $k=0$.[10] For $n=1$, 2, and 3, the binding energies are almost identical, 2.3 eV. These three binding energies are so similar because Cu_s induces no strain around it and H binds to Cu in a way that causes no strain either. As a result, the binding energy of H comes only from the formation of a covalent Cu-H bond.

Forming a Si-H bond at the antibonding site of a Si next to Cu would involve breaking one of the Cu-Si bonds ($\sim$0.7 eV) and displacing a Si atom to the plane of its nearest neighbors at some additional cost in energy. Thus, for the $\mathrm{Cu}_s\cdots\mathrm{Si}\text{-}\mathrm{H}_{\mathrm{AB}}$ configuration to become energetically favorable, its binding energy would have to exceed $2.3+0.7=3.0$ eV. Since H at the AB site of Si forms rather weak bonds, this configuration is simply not competitive (at least for copper).

The case of $\{\mathrm{Cu}_s,\mathrm{H}_4\}$ is different. At $T=0$ K, conjugate gradient calculations show that this complex does form with all four H's bound to Cu_s. The latter becomes eightfold coordinated (to four Si's and four H's). However, the binding energy ΔE_4 is only 0.6 eV and this complex is unstable. We performed several constant-temperature MD runs at various temperatures (room T to 1000 K). The runs invariably result in a break-up of $\{\mathrm{Cu}_s,\mathrm{H}_4\}$. In some runs, the Cu-H wag modes bring pairs of H's close to each other. This allows the H's to overlap and $\{\mathrm{Cu}_s,\mathrm{H}_4\}$ dissociates into Cu_s and two nearby interstitial H_2 molecules.[79] But in other runs, the complex breaks up into $\{\mathrm{Cu}_s,\mathrm{H}_3\}$ and a nearby H_{BC} or other combinations. Note that these MD runs are limited to a few ps real time, which is too short to reach equilibrium. However, all these runs confirm that $\{\mathrm{Cu}_s,\mathrm{H}_4\}$ is unstable. This instability is further illustrated by a comparison of the $\{\mathrm{Cu}_s,\mathrm{H}_n\}$ complexes with Cu_i and a partially or fully saturated vacancy: $\mathrm{Cu}_i+\{\mathrm{V},\mathrm{H}_n\}$ is less stable than $\{\mathrm{Cu}_s,\mathrm{H}_n\}$ by $\Delta E_n'=2.38$ eV ($n=1$), 1.54 eV ($n=2$), 1.31 eV ($n=3$), and 0.15 eV ($n=4$). The latter energy is very small indeed.

The vibrational spectra of the $\{\mathrm{Cu}_s,\mathrm{H}_n\}$ complexes ($n=1,2,3$) with D substitutions were obtained from linear response theory.[77] The calculated frequencies are given in Table I.

TABLE I. Local vibrational modes of the $\{\mathrm{Cu}_s,\mathrm{H}_n\}$ complexes with D substitutions. $\{\mathrm{Cu}_s,\mathrm{H}_1\}$ has C_{2v} symmetry, the other complexes have either C_s or C_1 symmetry.

	all H	one D			two D's		three D's
$\{\mathrm{Cu}_s,\mathrm{H}_1\}$	803	592					
	1904	1356					
$\{\mathrm{Cu}_s,\mathrm{H}_2\}$	705	579	588		545		
	949	871	851		686		
	1721	1227	1300		1225		
	1825	1824	1720		1299		
$\{\mathrm{Cu}_s,\mathrm{H}_3\}$	787	744	607	593		739	578
	980	793	975	752		724	718
	1104	1048	1082	1035		836	799
	1658	1273	1200	1187		1282	1180
	1767	1659	1767	1273		1257	1257
	1804	1785	1800	1783		1659	1282

IV. INTERACTIONS OF Cu_i WITH O

We also studied the interactions between Cu_i and either interstitial oxygen (O_i) or the $\{\mathrm{O,V}\}$ complex (A center[80]). The former is a bond-centered interstitial with D_{3d} symmetry (the energy difference between the straight and the puckered Si-O-Si bond is very small). The latter is off center in a vacancy, bound to two Si atoms (the other two Si dangling bonds reconstruct), and has C_{2v} symmetry. The A center is known to react with a number of impurities, in particular hydrogen.[81]

Cu_i^+ is attracted to O_i because oxygen locally distorts the crystal which results in an interstitial void near O_i larger than away from it. In the lowest-energy configuration, the O-Cu distance is 2.0 Å. The calculated binding energy (Cu_i^+ and O_i near each other v infinitely far apart) is 0.31 eV. This energy is quite close to the one measured from transient-ion-drift experiments, 0.20 ± 0.05 eV.[63] It is also very similar to the measured[82] 0.26 eV binding energy of an interstitial H_2 molecule trapped near O_i. In both cases there is no covalent overlap between O_i and interstitial Cu_i^+ (or H_2). None is expected since O_i is happily twofold coordinated and Si-O is one of the strongest chemical bonds in nature: O has no incentives to weaken (or break) a Si-O bond to form a much less energetic Cu-O bond (or overlap with an H_2 molecule). In diatomic molecules,[83] the bond strengths of Cu-O and Si-O are 2.7 and 8.0 eV, respectively.

A notable feature is that the Si-O-Si bond puckers when Cu_i^+ (or H_2) is nearby, and this strongly affects the vibrational spectrum. In the isolated O_i defect, the Si-O-Si bond angle is 180° and the calculated LVM's of O_i are the A_{2u} mode at 1133 cm^{-1} (measured:[80] 1136 cm^{-1}) and the A_{1g} mode at 608 cm^{-1} (measured:[80] 618 cm^{-1}). When H_2 traps near O_i, we find that the Si-O-Si bond puckers to 149° and the LVM drops to 1043 cm^{-1} (experimentally,[82] 1075 cm^{-1}). When Cu_i^+ is nearby, O_i puckers even more, with the Si-O-Si angle at 138° (O points toward Cu), and the stretch-mode frequency of O parallel to the trigonal axis drops to 886 cm^{-1}. A second LVM at 591 cm^{-1} has O_i vibrating along the O-Cu direction. These modes could be the signature of the $\{\mathrm{Cu}_i,\mathrm{O}_i\}^+$ complex. We need to point out that these frequencies strongly depend on the Si-O-Si angle, but the total energy varies very little with it. Further, these modes are expected to be highly anharmonic, but our calculations involves the harmonic approximation. Therefore, the error bar on the predicted numbers could be larger than average. Since the binding energy of Cu_i^+ to O_i is low, these modes should be observed only at low temperatures and if enough Cu can be diffused into a CZ-Si sample. Figure 2 shows the complex.

Cu_i^0 interacts more energetically with the A center than with O_i. We performed several MD runs at room temperature and 500 K to see how Cu_i, placed near the A center, reacts with it. The result of these simulations is that copper easily displaces O from the vacancy and becomes Cu_s while

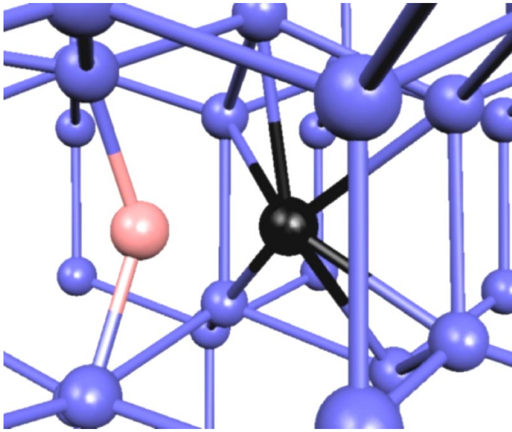

FIG. 2. (Color online) Cu_i^+ (black sphere) prefers to be at an interstitial site near O_i (light gray sphere) than far away from it by 0.31 eV, but only because of the extra free volume available. The population analysis shows no covalent Cu-O overlap.

O bridges an adjacent Si-Si bond. We label this the $\{Cu_s, O_i\}$ complex. The lowest-energy configuration does not occur when the two impurities are very far apart but when they remain close to each other: the energy difference between $\{Cu_s, O_i\}$ and Cu_s infinitely far apart from O_i is 0.44 eV. The reaction $Cu_i + A$ center$\rightarrow\{Cu_s, O_i\}$ releases 1.69 eV.

The $\{Cu_s, O_i\}$ complex is shown in Fig. 3. The Si-O-Si bond angle is 153° and the calculated asymmetric stretch along the trigonal axis is 1008 cm^{-1}. A second LVM at 588 cm^{-1} has O moving perpendicular to the Si-O-Si axis and its two Si neighbors along this axis.

V. INTERACTIONS OF Cu_i WITH A SELF-INTERSTITIAL

Since Cu_i^0 ejects O from the $\{O,V\}$ complex in order to become Cu_s, we wondered what would happen if Cu_i were placed near a Si self-interstitial (I). In its lowest-energy configuration, I is a split-$\langle 110\rangle$ interstitialcy, but the center of the split is shifted by 0.80 Å in the $\langle 001\rangle$ direction.[75] This

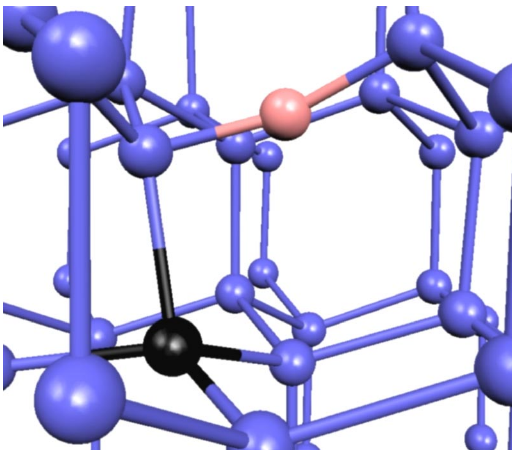

FIG. 3. (Color online) When near the *A* center, Cu_i^0 kicks O (light gray sphere) out of the vacancy, takes its place, and becomes Cu_s (black sphere). The lowest-energy configuration is the $\{Cu_s, O_i\}$ complex shown, with no covalent Cu-O overlap.

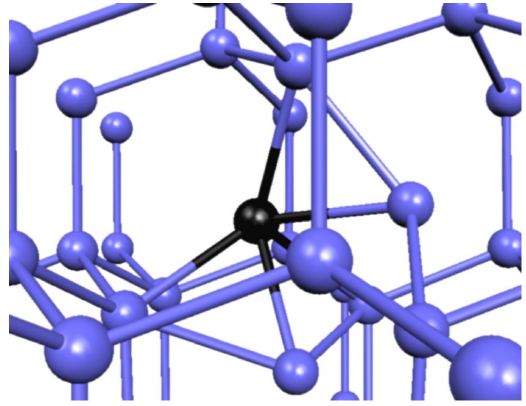

FIG. 4. (Color online) The interaction between Cu_i and a self-interstitial results in the formation of a complex which resembles $\{Cu_s, I_2\}$, but Cu (black sphere) is 1.2 Å away from the substitutional site while the two Si atoms are 1.6 Å away from it.

configuration leaves the perfect substitutional site quite open. We tested the possibility that Cu_i might jump into it. In other words, is the reaction $Cu_i + I \rightarrow Cu_s + I_2$ energetically favorable? The constant-*T* MD runs show that this is not fully realized. In the lowest-energy configuration (Fig. 4), copper is 1.2 Å away from the substitutional site while two (equivalent) Si atoms are 1.6 Å away from it. The complex has C_s symmetry and consists of an isosceles triangle in the $\{111\}$ plane, the center of which is 0.44 Å from the substitutional site. The energy of this complex is 1.59 eV lower than having I infinitely far away from Cu_i.

VI. SUMMARY AND DISCUSSION

The most abundant configuration of copper in Si is Cu_i^+, which can be introduced into the bulk in rather large concentrations at high temperatures ($\sim 10^{16}$ cm^{-3} at 1000°C). Upon cooling, it tends to precipitate or out-diffuse to the surface, but some of it remains as Cu_s. The present study deals with the interactions between copper and H, O, and the self-interstitial at low temperatures. Our first-principles MD simulations confirm the conclusions of earlier *ab initio* HF results[58] that copper in Si is a chemically active species with a surprising variety of covalent interactions.

Cu_s forms only when vacancies are provided. The reaction $Cu_i + V \rightarrow Cu_s$ releases ~ 2.8 eV, which is much less than the formation energy of the vacancy [~ 4 eV (Ref. 59)]. Cu_s is on-site and fourfold coordinated and its $3d$ electrons participate in the bonding. Each of the four Cu-Si bonds has a strength of ~ 0.7 eV. These are weak but covalent bonds.

Interstitial H is attracted to Cu_s and $\{Cu_s, H_n\}$ complexes form, with $n=1$, 2, and 3. The reactions $\{Cu_s, H_{n-1}\} + H_{BC} \rightarrow \{Cu_s, H_n\}$ occur at a gain of 2.3 eV for $n=1$, 2, or 3. These complexes differ from other impurity-hydrogen complexes in Si in a variety of ways. *First*, H binds directly to the TM, not to a Si atom near it. There is no H-Si overlap. *Second*, the binding energies (relative to isolated H_{BC}) are almost the same for $\{Cu_s, H_n\}$ with $n=1$, 2, and 3. The reasons for this are that Cu_s does not distort the surrounding host crystal, and therefore H does not have much strain to

relieve and its binding energy comes almost exclusively from the formation of Cu-H bonds. Thus, even if some {TM,H} complexes have H at the AB site of a Si atom adjacent to the TM (as predicted in Refs. 52–55), this configuration is not universal. The $\{Cu_s, H_4\}$ complex is unstable and MD runs show that it can dissociate in several ways. Interestingly, one of the possibilities is the dissociation into Cu_s and two nearby interstitial H_2 molecules. Thus, if enough H is present, Cu_s could become a machine that fabricates H_2. All the H- (and D-) related LVM's of $\{Cu_s, H_n\}$ (with $n=1$, 2, and 3) are predicted.

Cu_i^+ is attracted to O_i because of the slightly larger free volume available around the T site near O_i than far away from it. The small binding energy (0.3 eV) is close to the measured one[63] and to that of H_2 near O_i.[82] There is no Cu-O covalent overlap. However, the Si-O-Si bond puckers with O pointing toward Cu, and the O_i asymmetric stretch drops from 1133 to 886 cm^{-1} (calculated).

Cu_i reacts with the *A* center by "stealing" the vacancy and forcing O into an interstitial configuration. The reaction $Cu_i + \{O,V\} \rightarrow \{Cu_s, O_i\}$ releases 1.7 eV. The $\{Cu_s, O_i\}$ complex consists of a slightly off-center Cu_s and a puckered Si-O-Si with one Si adjacent to Cu. The asymmetric stretch of this O is at 1008 cm^{-1}.

The reaction $Cu_i + I \rightarrow \{Cu_s, I_2\}$ is only imperfectly realized, with Cu 1.2 Å away from the perfect substitutional site. The binding energy is 1.6 eV. Note that the precipitation of Cu at or near O precipitates, dislocations, and other defects has been reported (the most recent study is in Ref. 8). Our calculations involve a single Cu and a single O or I, and therefore describe a much simpler situation. Although we find that Cu tends to come close to O, there is no hint that a Cu-O bond can form. Instead, Cu binds rather strongly to I. Since O precipitation tends to release I's, sometimes leading to the formation of dislocation loops around O precipitates, our results suggest that Cu traps at I's near rather than at O precipitates.

The most energetic reactions we find are $Cu_i + V \rightarrow Cu_s + 2.8$ eV (V is a preexisting vacancy), then $\{Cu_sH_{n-1}\} + H_{BC} \rightarrow \{Cu_s, H_n\} + 2.3$ eV (with $n=1,2,3$), $Cu_i + \{O,V\} \rightarrow \{Cu_s, O_i\} + 1.7$ eV, and $Cu_i + I$ leading to a "$\{Cu_s, I_2\}$" complex at a gain of 1.6 eV. Cu_i^+ is weakly attracted to O_i (0.3 eV), and the $\{Cu_s, H_4\}$ complex is unstable.

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