PHYSICAL REVIEW B **72**, 121201(R) (2005)

$^{*}Cu_0$: A metastable configuration of the $\{Cu_s, Cu_i\}$ pair in Si

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(Received 25 April 2005; revised manuscript received 20 June 2005; published 1 September 2005)

First-principles theory shows that the substitutional-interstitial copper pair in Si (Si-$Cu_s\cdots Cu_i$) has a metastable state with Cu_i very near a tetrahedral interstitial site in a trigonal Cu_s-Si$\cdots Cu_i$ configuration that exhibits three low-frequency pseudolocal vibrational modes. The lowest of them, at 40 cm^{-1}, has A_1 symmetry and is the likely source of the phonon sidebands observed at 52 cm^{-1} in the photoluminescence band of a defect known as $^{*}Cu_0$.

DOI: 10.1103/PhysRevB.72.121201 PACS number(s): 61.72.Bb, 63.20.Pw, 71.55.Cn

Transition metal impurities of the 3*d* series are common contaminants in Si and are often associated with recombination centers.[1,2] Copper is the fastest diffusing transition metal in Si and reacts readily with native defects, dopants, and various impurities, including itself.[3–5] These interactions often affect the electrical and optical properties of the material. Photoluminescence (PL) and deep-level transient spectroscopy (DLTS) studies of copper pairs[4] in Si show the presence of two related defects labeled Cu_0 and $^{*}Cu_0$, respectively. Cu_0 has been identified as the substitutional-interstitial $\{Cu_s, Cu_i\}$ pair, but $^{*}Cu_0$ has yet to be identified. In this paper, we present theoretical evidence that a metastable configuration of this pair exists and that its calculated properties are consistent with those of $^{*}Cu_0$.

The PL band[6,7] of Cu_0 is characterized by a zero-phonon line at 1014 meV and sharp anti-Stokes phonon sidebands separated by 7.05 meV, indicative of a pseudolocal vibrational mode (pLVM) at 57 cm^{-1}. Very weak additional phonon replicas at 16.4 and 25.1 meV (132 and 202 cm^{-1}, respectively) have also been reported[8] in the PL spectrum. The Cu_0 defect[7,9,10] is isoelectronic, exhibits trigonal symmetry under uniaxial stress, and consists of two copper atoms. The PL band has been correlated[11] with a DLTS center at E_v +0.100 eV. The dissociation enthalpy of the defect in the temperature range 333–417 K (Ref. 12) is 1.02±0.07 eV. Since the migration energy[13] of Cu_i^+ is 0.18±0.02 eV, the binding enthalpy in that temperature range is 0.84±0.09 eV.

First-principles theory[14] predicts that the $\{Cu_s, Cu_i\}$ pair has trigonal symmetry and a binding energy of 1.16 eV at $T=0$ K. When the vibrational free energy and configurational entropy are included,[15] this number drops to 0.94 eV at 373 K, in agreement with the measured value. The vibrational spectrum of the pair shows a pLVM with A_1 symmetry at 62 cm^{-1}. In this mode, the three atoms (Si-$Cu_s\cdots Cu_i$) move together along the trigonal axis with constant Cu–Cu bond length. Thus, the calculated properties of the neutral $\{Cu_s, Cu_i\}$ pair are quantitatively consistent with the key features observed for the Cu_0 defect.

Isolated bond-centered interstitial copper has been proposed[16] for Cu_0. However, our calculations show that this configuration is not stable: If copper is placed at a relaxed bond-centered site, conjugate gradient geometry optimizations[14] show that copper is ejected from this site, stabilizes at the tetrahedral interstitial (T_i) site, and the perturbed Si–Si bond is fully restored. The only interstitial site for isolated copper in Si is the T_i site.

The origin of the $^{*}Cu_0$ center is far less clear. Its PL band[17,18] has a zero-phonon line at 944 meV assigned to the excitonic recombination of an isoelectronic center. Phonon replicas separated by 6.42 meV indicate a pLVM at 52 cm^{-1}. The ionization cross section of the defect has recently been measured.[19] The 944 meV band appears to be associated with a DLTS level at $E_v+0.185$ eV.[20,23] The $^{*}Cu_0$ defect is long-lived at room temperature. In melt-doped samples with high concentrations of Cu_s, etched with a Cu-containing solution, the concentrations of both $^{*}Cu_0$ and $\{Cu_s, Cu_i\}$ pairs (as measured by DLTS) decrease with depth while the concentration of isolated Cu_s increases with depth. This suggests that Cu_s is involved in both centers.

$^{*}Cu_0$ is seen in samples with low copper concentrations,[17] in samples annealed at high temperatures,[20,21] and in dislocated samples.[20] The $^{*}Cu_0$ PL band sometimes coexists with that of the $\{Cu_s, Cu_i\}$ pair in the same sample. The role of dislocations in the formation of $^{*}Cu_0$ is unclear. They affect the concentrations of vacancies and self-interstitials, which led to the suggestion[22] that native defects could be involved. However, dislocations may simply be serving as traps for Cu_i, thus reducing the amount of free Cu_i. In this case, "dislocated samples" become equivalent to "low Cu," but neither of these statements is unambiguous or quantitative. The intensity of the $^{*}Cu_0$ PL band also depends on the quench rate.[17]

Uniaxial stress and Zeeman splitting studies[18] of $^{*}Cu_0$ suggest *T*-to-*A* transitions in T_d symmetry. The authors tentatively proposed that $^{*}Cu_0$ could be isolated Cu_i^+ at the T_i site. There are several problems associated with the proposed tetrahedral symmetry for $^{*}Cu_0$. Only two copper defects in Si have T_d symmetry: Cu_s and Cu_i. We can rule out isolated Cu_s as a plausible candidate since its well-known DLTS spectrum is distinct from that of $^{*}Cu_0$. Further, melt-doped samples that contain only Cu_s do not show the PL band of $^{*}Cu_0$. Then, first-principles calculations[14] show no pLVM associated with isolated Cu_s. Finally, the fully symmetric mode in T_d symmetry is the breathing mode of the four Si neighbors to Cu_s, a highly unlikely source of sharp phonon replicas. Although complexes containing five Cu_s (or Cu_i) or one Cu_s with four adjacent Cu_i's (or vice versa) could also have T_d symmetry, it is difficult to imagine how such centers would

preferentially form in samples containing low copper concentrations. One should also rule out Cu_i as a plausible candidate for $^*Cu_0$. Interstitial copper readily precipitates or outdiffuses at temperatures at which the $^*Cu_0$\PL band is stable. Further, no DLTS signature of Cu_i has been reported to date. Its donor level is assumed to be either in the conduction band or resonant with it. Then, theory predicts[14] that the lowest-lying pLVM associated with Cu_i is a triplet around 150 cm^{-1}, which is not only much too high in frequency but also unlikely to give rise to sharp phonon replicas. The uniaxial stress studies need to be repeated at higher stress values. The proposed assignment of isolated Cu_i as a candidate for the $^*Cu_0$ defect has recently been questioned[19] by the experimental group that first suggested it.

In this paper, we perform first-principles calculations based on local density-functional theory as implemented in the SIESTA code.[24,25] The exchange-correlation potential is that of Ceperley-Alder[26] as parametrized by Perdew and Zunger.[27] Norm-conserving pseudopotentials in the Kleinman-Bylander form[28] are used to remove the core regions from the calculations. The basis sets for the valence states are linear combinations of numerical atomic orbitals.[24,29,30] Double-zeta polarized basis sets are used throughout: two sets of valence s and p's plus one set of d's on all the atoms. 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 from 50 to 250 Ry confirm that this cutoff is sufficient. The host Si crystal is represented by 64 and 128 host atoms periodic supercells, and a $2\times2\times2$ Monkhorst-Pack[31] mesh is used in the smaller cell. The matrix elements of the (harmonic) dynamical matrices are extracted at $T=0$ K from the derivatives of the density matrix relative to nuclear coordinates using the perturbative approach[32,33] implemented into SIESTA by Pruneda *et al.*[34] The dynamical matrices are calculated at $k=0$.

The eigenvalues of the dynamical matrix are the normal-mode frequencies of the cell and the eigenvectors give the relative displacements of all the atoms for each normal mode. Thus, from the (normalized) eigenvectors, one obtains the square of the relative amplitude $A^2(Cu_s+Cu_i)$ of the oscillation of the two Cu atoms for each normal mode. This amplitude is zero or very small for crystal phonons but large for modes involving substantial motion of the Cu atoms. Once the frequencies of these pLVMs are identified, the corresponding eigenvectors provide the symmetry of the modes, which is critical to determine whether they can give rise to phonon replicas in PL bands. This approach has been used to identify the pLVMs associated with the $\{Cu_s,Cu_i\}$ pair.[14]

Conjugate gradient geometry optimizations show that the $\{Cu_s,Cu_i\}$ pair (Si-$Cu_s\cdots Cu_i$) forms without barrier when Cu_i is placed at the nearest or a second-nearest T_i site to Cu_s. A metastable configuration of the pair occurs when Cu_i is at one of the four T_i sites located in the antibonding direction of a Cu_s–Si bond, in a trigonal Cu_s-Si$\cdots Cu_i$ configuration (Fig. 1). Note that in the 64 host-atoms cell, Cu_i moves off the T_i site resulting in a defect with overall C_1 symmetry. However, this is a cell size effect: The symmetry of this defect is perfectly trigonal in the 128 host-atoms supercell and remains trigonal in the 216 host-atoms cell.

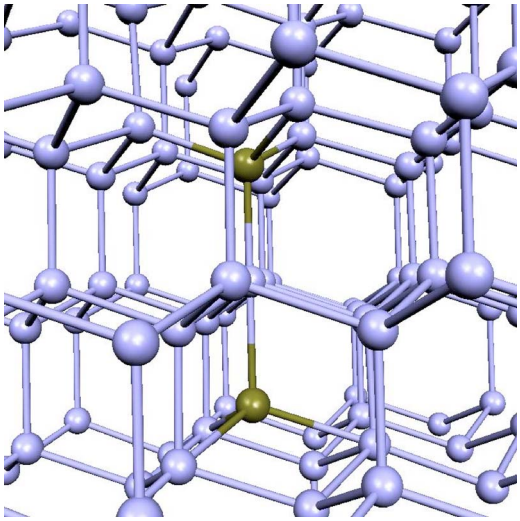

FIG. 1. (Color online) The metastable configuration of the neutral copper pair in Si has Cu_i at a T_i site along the antibonding direction of a Cu_s–Si bond, in a trigonal Cu_s-Si$\cdots Cu_i$ configuration. The Si atoms are the light gray spheres (blue) and the Cu atoms are the darker gray spheres (gold).

We calculated the binding energy of the metastable configuration relative to isolated Cu_s^- and Cu_i^+ at three levels of theory. In the 64 host-atoms cell with double-zeta polarized basis sets on all the atoms and a $2\times2\times2$ k-point mesh, we get 0.41 eV. The same calculation, but with polarization functions, only on the copper atoms gives 0.51 eV. In the 128 host-atoms cell with a double-zeta polarized basis set everywhere but a $1\times1\times1$ k-point mesh, the binding energy is 0.63 eV. Note that the Cu_s^- and Cu_i^+ calculations in periodic supercells have an uncertainty associated with the spurious Madelung energy contribution.[35] The error is vanishingly small if the charge (like the compensating background charge) is uniformly distributed in the cell, and of the order of 0.13 eV (0.26 eV) in the 128 (64) atoms cell for a point charge with a uniform background. Thus, the uncertainty in the 128 atoms cell is rather small. Further, the binding energy calculated here is to be compared to that of the $\{Cu_s,Cu_i\}$ pair, also calculated[14] relative to isolated Cu_s^- and Cu_i^+, without a Madelung correction. Thus, the binding energy of the Si-$Cu_s\cdots Cu_i$ is about half that of the stable $\{Cu_s,Cu_i\}$ pair. The dissociation energy is larger by 0.18 eV, the migration energy[13] of Cu_i^+.

The dynamical matrices of the stable ($\{Cu_s,Cu_i\}$) and metastable (Fig. 1) copper pairs in the neutral charge state show the existence of a pLVM with A_1 symmetry for both complexes. The relative amplitudes squared of the oscillations of the two copper atoms for both pairs are shown in Fig. 2. The dynamical matrix of the stable pair (Si-$Cu_s\cdots Cu_i$) was calculated in the 64 atoms cell, Ref. 14, and that of the metastable pair (Cu_s-Si$\cdots Cu_i$) in the 128 host-atoms cell. In the stable configuration, the vibrational spectrum shows a pLVM with A_1 symmetry at 62 cm^{-1}. In this mode, the Si and the two Cu atoms move along the trigonal axis together, with constant Cu_s–Cu_i bond length. The metastable complex has a similar mode at 40 cm^{-1}, which involves the motion of the same three atoms, but Si is between the two Cu.

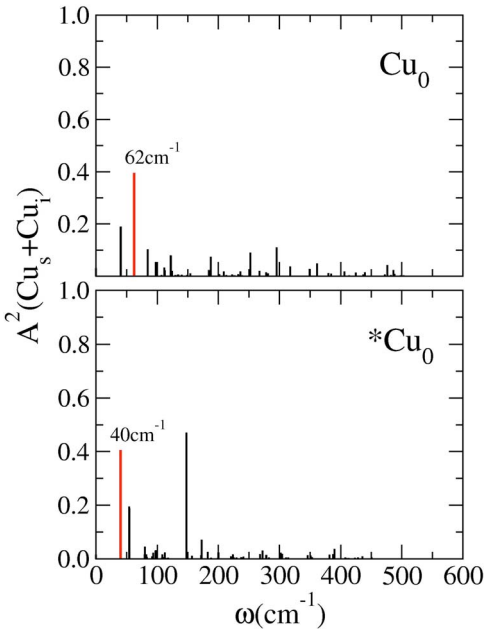

FIG. 2. (Color online) Square of the relative oscillation amplitude of the two Cu atoms vs normal mode frequency for the stable Si-$Cu_s\cdots Cu_i$ (calculated in the 64 host-atoms supercell) and metastable Cu_s-Si$\cdots Cu_i$ (calculated in the 128 host-atoms supercell) configurations of the copper pair in Si. The modes are described in the text. Note that the amplitudes shown are obtained from the eigenvectors of the dynamical matrix and do *not* include the expectation value of the dipole moment operator.

In both cases, the effective mass of the oscillator is the same but the spring constants differ since the Cu_s–Cu_i and Si–Cu_i bonds are inequivalent. Since the Si atom oscillates together with the two Cu atoms, we expect the ^{30}Si isotope effects to be smaller than measurable. Indeed, our calculations show that the 40.2-cm^{-1} phonon sideband will shift to 39.6 cm^{-1}, a shift too small to be observable. The asymmetric Cu_i–Si stretch is at 390 cm^{-1}, unlikely to be observable by PL (or infrared absorption spectroscopy). The degenerate modes at 54 cm^{-1} (Fig. 2) are wag modes with Cu_i and, to a smaller extent, Cu_s, moving perpendicular to the trigonal axis, with a small motion of the central Si atom. Three additional pLVMs at 147 and (two at) 148 cm^{-1} are a stretch mode with the Cu atoms moving in opposition to each other and the corresponding wag modes, respectively. The 147-cm^{-1} mode could be hidden in the third phonon sideband of the PL spectrum.

In conclusion, we provide theoretical evidence that two configurations of the substitutional-interstitial copper pair exist in Si, both with C_{3v} symmetry. The stable one, Si-$Cu_s\cdots Cu_i$, has E_b=1.16 eV and a pLVM with A_1 symmetry at 62 cm^{-1}. It has been identified[14] as the Cu_0PL center, which has phonon sidebands at 57 cm^{-1}. The metastable Cu_s-Si$\cdots Cu_i$ pair has E_b=0.63 eV and exhibits a pLVM with A_1 symmetry at 40 cm^{-1}, close to the observed sidebands at 52 cm^{-1}. In both configurations, the same three atoms (Si, Cu_s, and Cu_i) move along the trigonal axis, a qualitative feature that is consistent with the remarkable similarity between the two PL bands. We do not expect an easy metastable-to-stable conversion since this would require Cu_i to migrate all around the defect, from the antibonding site of Si to the antibonding site of Cu_s. These two sites are 7 Å apart on a straight line but a much longer diffusion path is required.

Note that the Si-$Cu_s\cdots Cu_i$,Cu_s-Si$\cdots Cu_i$, and isolated Cu_s defects have DLTS levels at E_v+0.100, 0.185, and 0.20 eV, respectively, as if Cu_i perturbed the same level less and less as it is located further and further away from Cu_s. At this time, first-principles theory cannot predict DLTS levels with the desired accuracy to confirm this (the expected accuracy[36] of the best calculations is ±0.20 eV). Nevertheless, the Cu_s-Si$\cdots Cu_i$ complex is a strong candidate as the *Cu_0 PL center. The unresolved experimental issues deal with the symmetry of this center and the conditions under which it forms.

This work was supported in part by the R.A. Welch Foundation, the National Renewable Energy Laboratory, and the Alexander von Humboldt Foundation. Many thanks to Texas Tech's High Performance Computer Center for generous amounts of computer time.

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