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Subcontractor Report

Research in Hydrogen Passivation of Defects and Impurities in Silicon

Final Report
10 February 2000–10 March 2003

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Background

Several PV manufacturers commercially use the passivation of impurities and defects by H to improve the performance of their solar cells. There is however a severe lack of basic understanding of such issues as the interactions of H with transition metals, which strongly affect solar cell performance, the role of native defects (vacancies, self-interstitials, and their aggregates), the trapping of H at native defects, and even the nature of the defects that need to be passivated. The identification of the most important defects cannot rely on microscopic experimental tools alone. Electrical methods such as DLTS provide little insight into the microscopic nature of the defects. Vibrational spectroscopy is quantitative, especially when used in conjunction with isotope substitutions and uniaxial stress experiments. However, most IR lines in poly-Si are quite broad and it is not always possible to find samples with the needed concentration of a given defect for detail study.

Theory complements such experimental methods if it is 'first-principles' (no parameters fitted to experimental data) and able to predict measurable properties quantitatively (within a few %). The properties of interest include the geometry (in particular the symmetry), the local vibrational modes associated with the defect, as well as the binding and various activation energies. Today's theoretical 'state-of-the-art' involves periodic supercells to represent the host crystal and density-functional (DF) theory with ab-initio pseudopotentials to calculate the total electronic energy. Molecular-dynamic (MD) simulations allow the atomic nuclei to move in real time following classical mechanics, with forces calculated from the gradients of the total energies.

Objectives

The objectives of the research under this contract is to perform systematic first-principles calculations on native defects and selected transition metal impurities in Si and their interactions with hydrogen. One goal is to gain insight into which defects need to be passivated and which ones do not, which defects are the most stable, how interactions with H affect their electrical and optical properties. This includes potential surface and electronic structure calculations as well as real-time, constant-temperature, MD simulations to test the thermal stability of various defects and monitor defect reactions and/or diffusion. Another goal is to predict the local vibrational modes (LVMs), the binding and various activation energies of the most important H complexes, and other quantities which have been or can be measured experimentally. Further, theory itself needs to be continuously developed in order to allow more accurate predictions and the calculation of quantities that are beyond the reach of today's 'state-of-the-art'. The following issues are discussed in this report.

1. The interactions between vacancies (V) lead to the formation of V_n clusters, and these clusters are not all 'vacancy-like'. In particular, the hexavacancy (V_6) was predicted to be electrically inactive (earlier NREL project), but interactions with H render it optically active, and recent experimental data have now confirmed the earlier theoretical predictions.

2. The interactions between self-interstitials (I) result in the formation of I_n clusters. We identified the most stable ones and studied their surprising dynamics and interactions with hydrogen. In particular, the very stable I_3 cluster is incredibly mobile.

3. The static and dynamic properties of the interstitial H_2 molecule in Si have been calculated. These molecules are plentiful in many samples and constitute a source of 'hidden' hydrogen. They have been seen by IR and Raman spectroscopies.

4. Theory developments include the calculation of entire dynamical matrices. This allows the calculation of pseudo-LVMs and the characterization of the localization of the modes. Further developments are under way.

5. Our model transition metal impurity is copper. The present studies involves interstitial copper, its interaction with native defects (V and I), its interactions with itself (Cu pairs), with interstitial O and the A center (O-V pair), and with H. The results include the first identification of pseudo-LVMs, seen experimentally as phonon sidebands in photoluminescence spectra.

Methodology

The electronic densities and energies are obtained from self-consistent, first-principles DF theory within the local density approximation. The MD simulations are use Sankey's 'ab-initio-tight-binding' approach[1,2] as implemented in the SIESTA code.[3,4] The exchange-correlation potential is that of Ceperley-Alder,[5] parameterized by Perdew and Zunger.[6] Norm-conserving pseudopotentials in the Kleinman-Bylander form[7] are used to remove the core region from the calculations. The valence states are described by numerical linear combinations of atomic orbitals which allow the inclusion of multiple-zeta orbitals and polarization states. The charge density is projected on a real space grid with equivalent cutoffs of 100 to 150*Ry* to calculate the exchange-correlation and Hartree potentials. Large cutoffs are needed to describe localized states, such as the *d* states of copper. The host crystal is represented by periodic supercells of 64, 128, or 216 host atoms. The *k*-point sampling ranges from the Γ point only to a 2x2x2 (or even 3x3x3) Monkhorst-Pack mesh.[8]

The vibrational properties are calculated using linear response theory. The idea[9] is to calculate the entire dynamical matrix from the derivatives of the density matrix relative to nuclear coordinates. After the diagonalization, the eigenvalues of the dynamical matrix are all the normal frequencies of the cell. Its eigenvectors give the relative displacements of the atoms for each mode.

MD simulations are performed using DF quantum-mechanical forces. The ions are classical particles while the electrons remain at 0K on the Born-Oppenheimer surface (no electronic excited states). The temperature of the cell is related to the kinetic energy of the ions. MD runs can be done at constant temperature to check for defect diffusion or reaction. Variable temperature runs are useful for simulated quenching (or annealing). Runs at T=0K (conjugate gradients) force the system to converge toward the nearest minimum of the potential energy surface. The time step varies from 2.0*fs* to 0.2*fs,* depending on the mass of the lightest atom in the cell. Many thousands of time steps are needed for meaningful constant-temperature simulations.

Results 1: Native defects: vacancies

The vacancy in Si has deep levels in the gap which are efficient recombination centers. This is usually not a major problem since the equilibrium concentration of vacancies is low up to several hundred degrees Celsius. However, a number of common processes are know (or believed) to inject high-concentration of vacancies into the bulk: ion implantation or the deposition of some surface layers are two examples. These vacancies interact with impurities, and/or diffuse out of the sample, and/or interact with each other. The latter results in the formation of vacancy clusters V_n. As part of a previous project funded by NREL, we studied the structures, electronic properties, and binding energies of the most stable clusters.[10,11] One key prediction was that a particularly stable defect occurs when an entire hexagonal ring is missing from the crystal. This hexavacancy reconstructs so well that no energy level remains in the gap, except for an empty level near the bottom of the conduction band. This defect should therefore be invisible to electrical techniques, but was predicted to

be a strong gettering center for TM impurities such as H or Cu.[12] Once decorated with Cu, the defects becomes electrically active and detrimental to PV performance.

The experimental proof of this nearly-invisible defect was difficult to find. However, the empty level of V_6 near the conduction band makes it visible by photoluminescence (PL). Under illumination, an electron traps in this level, the defect becomes negatively charged, traps a hole in a wide orbit, and the recombination of the exciton provides a PL signature. The zero-phonon line shifts when V_6 traps hydrogen. Three previously unassigned PL band, B^4_{80}, B_{41}, and B^1_{71}, have now been identified with V_6 and two distinct $\{V_6,H,H\}$ defects.[13]

The figures below show (left) the binding energies $\Delta E_n = E(V_n) - E(V_{n-1}) - E(V_1)$ as well AS (right) the unreconstructed and reconstructed V_6 and the two $\{V_6,H,H\}$ defects. This is one example of an electrically inactive defect which is activated by trapping impurities.

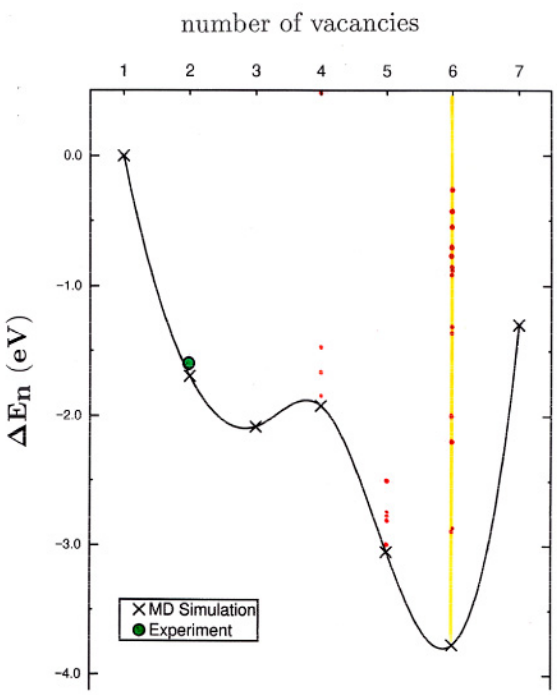


Fig. 1: Binding energies for vacancy clusters (see text).

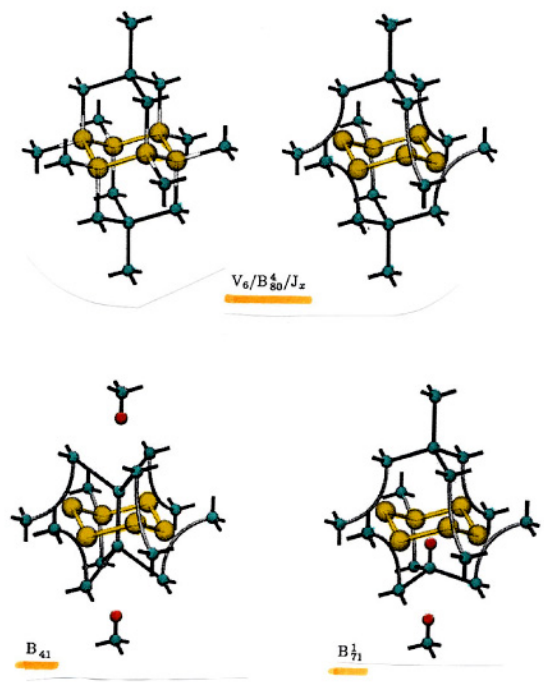


Fig. 2: V_6 and two $\{V_6,H,H\}$ complexes correspond to three previously unidentified PL bands.

Results 2: Native defects: self-interstitials

Systematic investigations[14] of self-interstitial (I) clustering also led to unexpected results. The (stable and metastable) configurations and binding energies of I_2, I_3, I_4, etc. show that one of two trigonal structures of I_3 is particularly stable. We labeled it I_{3a}. This defect, shown in Fig. 3, is centered at a bond-centered (BC) site. The most fascinating of its properties is not its high stability but the fact that it is highly mobile. We performed constant-temperature (first-principles) MD simulations on this and the other I_n clusters. To our surprise, once formed, the I_{3a} cluster diffuses faster than anything we have even seen in MD simulations. A sketch of the diffusion process is illustrated in Fig. 4.

Thus, as soon as I_{3a} forms, it becomes the fastest-diffusing defect known. This is a new possible explanation as to why the Si self-interstitial has never been observed. As soon as the I concentration is high enough for experimental studies (e.g. following Si implantation), self-interstitials are supersaturated. I+I gives I_2 then I_3. The latter diffuses

much too fast to be detected and possibly interacts with substitutional impurities such as B or C, or even precipitates into larger structures. Until now, it has been assumed that I diffuses very fast through a recombination-enhanced process or the Bourgoin-Corbett mechanism, but no firm evidence for these exotic processes has been found to date.

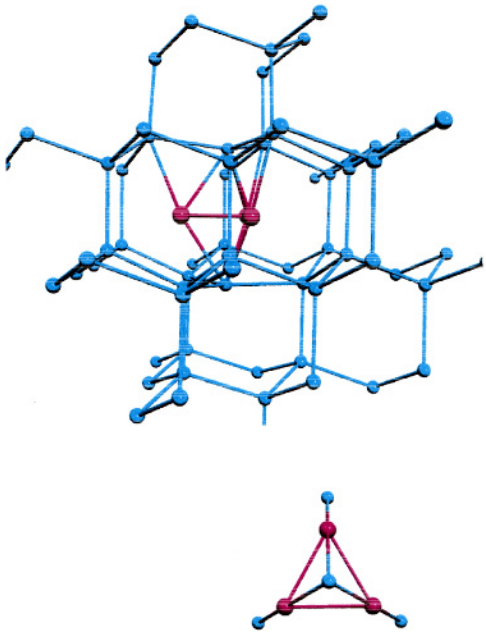


Fig. 3: Side and top views of the I_{3a} complex. It is an equilateral triangle in the {111} plane, centered at a bond-centered site. Note that only two host Si atoms are displaced from perfect substitutional sites.

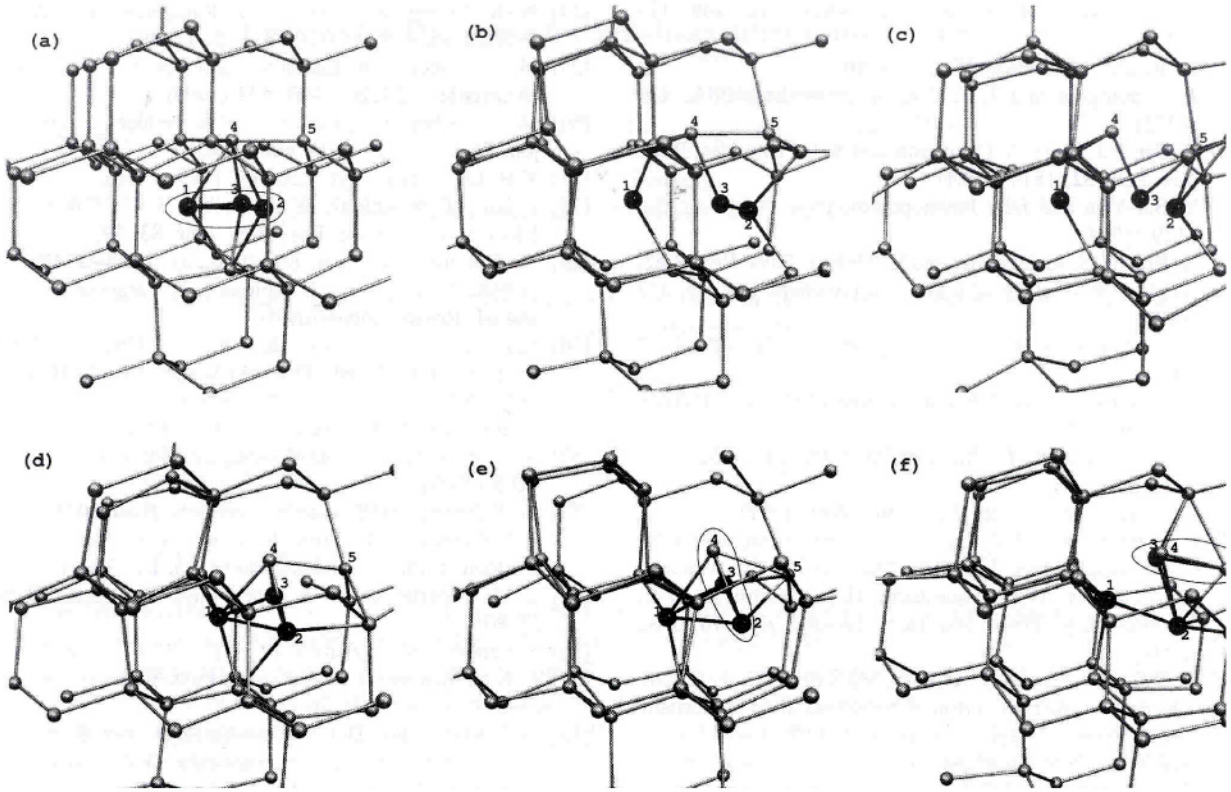


Fig. 4: The I_{3a} complex diffuses by successive exchanges (or kick-out processes) involving one of the self-interstitials and one of its host Si neighbors. The kickout is highly efficient, and the defect hops from one BC site to the next at the picosecond time scale. About 800 time steps at 1,000K separate Fig. (a) (in which I_{3a} consists of atoms 1,2 and 3) from Fig. (e) (in which I_{3a} consists of atoms 2, 3 and 4).

We investigated the possibility that I_3 plays an important role in self-interstitial precipitation by studying the reactions $I_3+I_3 \rightarrow I_6$, then $I_3+I_3 \rightarrow I_9$. In both cases, the reactions release several eVs, but only if the I_3's approach the defect along specific crystallographic directions.[15] These directions are consistent with the symmetry of the {113} self-interstitial rods (see e.g. [16]).

Finally, we studied self-interstitial-hydrogen complexes.[17] Up to four Hs can trap at or near a single I. The first two Hs are strongly bound (~1.8eV) and additional ones simply relieve the strain around the defect (~1.0 to 1.4eV). One interesting feature is that the odd electron wavefunction becomes increasingly delocalized as the size of the defect grows. Although the band-structures obtained from local density-functional theory are only qualitative, a comparison (Fig. 5) of the band structure of the perfect cell to the cell containing one self-interstitial or the {I,H,H} complex suggests that I induces a rather well localized level in the gap, and that this level is passivated after trapping two H interstitials and forming {I,H,H}.

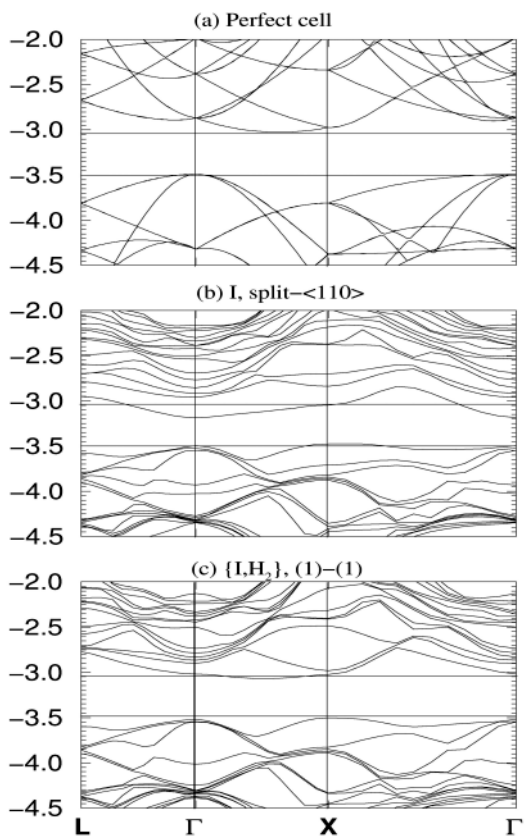


Fig. 5: Band structures of the perfect Si_{64} supercell (top) compared to that containing a self-interstitial (middle, showing the presence of an energy level below the conduction band minimum) and to the {I,H,H} complex, predicted to be passivated. The incorrect gap size (about half the measured value) is a consequence of the local density approximation. The band structures are qualitative.

Results 3: Interstitial H_2 molecules

Interstitial H_2 molecules in Si have been assumed to exist but observed experimentally only recently (for a review and references, see Ref. [18]). First-principles molecular dynamics simulations show that this molecule rapidly bounces around a tetrahedral interstitial (T) site (Fig.6). The vibrational frequencies calculated from the velocity-velocity autocorrelation function are very close to the measured ones.[19,20]

The theoretical results first appeared to contradict the experimental evidence. Indeed, uniaxial stress data were consistent with a low symmetry for the defect. Further, the absence

of ortho/para splitting in the spectra suggested that the molecule was not free to move (and rotate) but that its axis had to be fixed along a very low-symmetry direction. However, careful annealing studies demonstrated that only ortho-H_2 was IR active and that the apparent low symmetry was associated with the splitting of the J=1 rotational states by the applied stress rather than the actual symmetry of defect.[21,22]

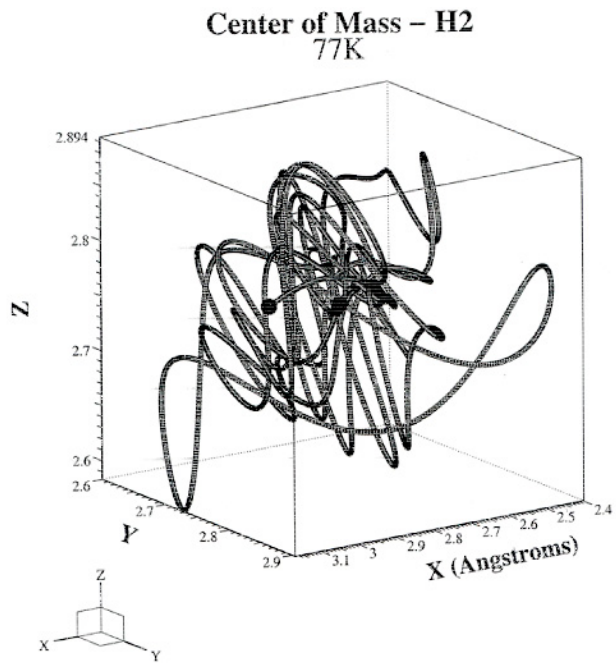


Fig. 6: Calculated position of the center of mass of the interstitial H_2 molecule near a T site in Si. The calculations involve 12,000 time steps at T=77K. The potential energy is very flat and this allows H_2 to rapidly bounce around. Note the sharp changes of direction. The side of the parallelepiped is of the order of 0.5Å, but the nearest Si atom is 2.35Å away from the center of the cube.

Results 4: Advances in methodology

A fruitful collaboration with a Ph.D. student from Oviedo (Spain) has substantially increased our ability to calculate the vibrational properties of defects in Si. The harmonic dynamical matrix (DM) is extracted directly from the first-order change in the density matrix with respect to infinitesimal atomic displacements from the equilibrium configuration.

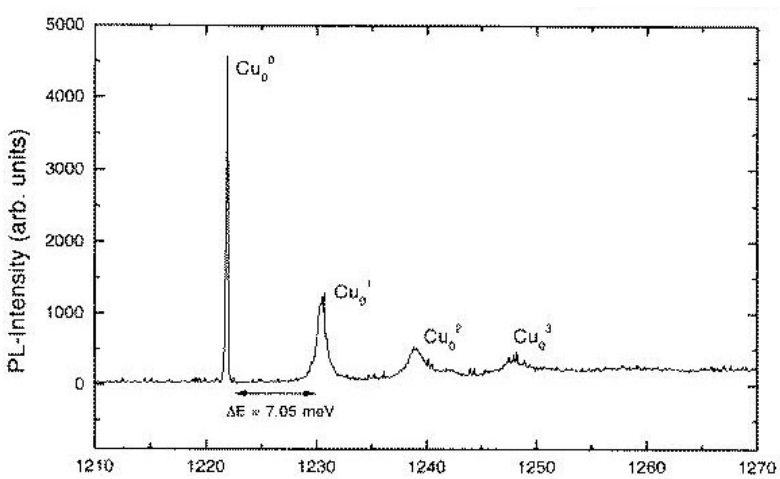
The eigenvalues of the DM are the normal frequencies of the cell, and its eigenvectors give the relative displacements of all the atoms for a particular vibrational mode. This approach was tested[9] for about 60 known local modes associated with various light impurities (H, B, C, O). The calculated frequencies turned out to be the most accurate available in the literature, with an average error bar of less than 2% for stretch modes, and 5-6% for the most anharmonic wag modes. We have since expanded the testing to some 100 modes and used the method to characterize the localization of pseudo-local vibrational modes (pLVMs), as discussed in section 5 below.

Much more than just vibrational frequencies and localizations can be extracted from the DM. At this time, we are exploring the construction of a phonon density of states (perturbed by a defect) which leads to the calculations (from first principles) of vibrational entropies and free energies. Another possible expansion would be the calculation of vibrational lifetimes and decay modes.

Results 5: Transition metal (TM) impurities: copper in Si

Copper is one of the most common TM impurities in Si, often introduced during chemomechanical polishing or metallization. It is also a good test case for theory because the *3d* shell of atomic Cu is full, and one need not worry about high spin multiplicities. Further, some microscopic experimental information is available on interstitial and substitutional copper, copper pairs, copper-hydrogen complexes, and copper-oxygen interactions. In *p*-type and intrinsic Si, most of 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[23] to be less than 0.24eV and measured[24] at 0.18±0.02eV. The solubility of copper in Si is low, and it tends to precipitate at/near vacancy-like defects, stacking faults, grain boundaries, and (some) dislocations. The key new results obtained during the period of this contract can be summarized as follows.

We have identified[25] with a high degree of certainty the defect associated with the substitutional/interstitial copper pair $\{Cu_s,Cu_i\}$. The experimental evidence includes the symmetry of the complex (from uniaxial stress), its dissociation energy (from thermal anneals), and an elusive photoluminescence (PL) band called 'Cu^0' in which the zero-phonon line is accompanied by sharp phonon replicas, indicative of a low-frequency vibrational mode which is localized despite being buried deep in the phonon band, at 57 cm^{-1}. It is not unusual for TM complexes to show PL activity which includes such sidebands, but none have been identified to date. Our calculations show that *(i)* the $\{Cu_s,Cu_i\}$ pair is trigonal, *(ii)* its binding energy is 1.16eV, and *(iii)* there exists a pseudo-local mode with the right symmetry at 68cm^{-1}. Note that ongoing (fist-principles) calculations of free energies show that the calculated binding energy converges toward the measured dissociation energy at higher temperatures. Note also that the pseudo-LVM calculations are the very first of their kind. Figure 7 shows the PL spectrum of the $\{Cu_s,Cu_i\}$ pair (left) and the pair itself. The vibrational mode responsible for the phonon replicas has both Cu atoms moving together along the trigonal axis, a motion that preserves the Cu-Cu bond length.



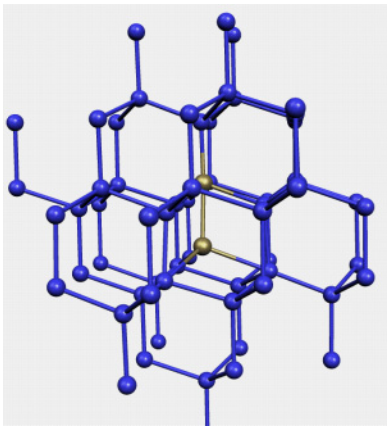


Fig. 7: The phonon sidebands visible in the PL spectrum of the 'Cu0' defect (left) are caused by a vibrational mode of the {Cus,Cui} pair (right) in which both Cu atoms move together as a unit along the trigonal axis.

We also showed[26] that substitutional copper can trap up to three H interstitials. Hydrogen always binds directly to the TM, not in the antibonding ($TM—Si—H_{AB}$) configuration proposed by other authors.[27] The structures of $\{Cu_s,H_1\}$, $\{Cu_s,H_2\}$,

$\{Cu_s,H_3\}$, are shown in Figure 8. All the LVMs associated with the $\{Cu,H_n\}$ complexes and their D substitutional have been calculated to help with future IR investigations. The binding energies of these complexes are of the order of 2.3eV.

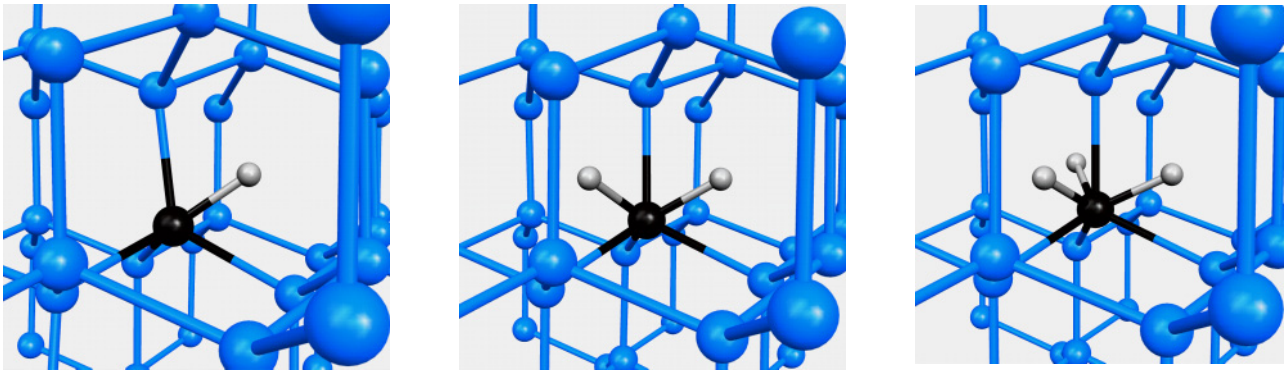


Fig. 8: Calculated configurations of the $\{Cu_s,H_n\}$ complexes with n=1, 2, and 3. In contrast to common assumptions, H does not bind to a Si atom near the TM but to the TM itself.

Interstitial copper (Cu_i) is attracted to oxygen in Si, but the interactions never result in the formation of Cu-O bonds.[26] Cu_i weakly traps (0.3eV) near interstitial oxygen (O_i) because the local lattice distortion around O results in a larger interstitial volume for Cu. This binding energy is very close to the one extracted from Cu diffusivity measurements in FZ (O-poor) vs. CZ (O-rich) material: in CZ-Si, copper slows down due to a weak trap. We predicted a shift in the oxygen-related LVMs associated with the trapping of Cu (this should be observable at low temperatures).

Cu_i also interacts with the oxygen-vacancy pair (also known as the A-center) but the reaction is unexpected: $Cu_i + \{O,V\} \rightarrow Cu_s + O_i$. Copper pushes O out of the vacancy and takes its place, leaving a complex with Cu_s slightly off-center and O_i bridging an adjacent (puckered) Si-Si bond. This reaction releases 1.7eV.

Finally, we showed that Cu binds to self-interstitials (E_b=1.6eV). These results suggest that Cu does not trap *at* O precipitates but *near* them, more precisely at the self-interstitials that are generated by the O precipitation and cluster around them, sometimes forming dislocation loops. There is evidence of copper gettering near oxygen precipitates, but no evidence of the formation of Cu-O bonds.[28]

Summary and conclusions

The key theoretical results obtained during this project and their significance to the PV community can be summarized as follows.

1. Vacancy-like defects do not always behave like vacancies should. If a defect can reconstruct efficiently, its electrical activity is substantially reduced or even suppressed. However, some strain remains and the defect easily becomes a gettering center for impurities (H and Cu have been studied). After trapping impurities, the system becomes electrically active again. It has been know for some time that some defects in solar cells are 'good' while others are 'bad', and that 'good' defects can become 'bad' when impurities trap at them. The research done here provides the first example of such a defect, with all the needed microscopic characterization. This implies that the history of a sample may be crucial and

that the order in which various processing steps are done may affect the efficiency of the finished cell.

2. If a process generates a high concentration of self-interstitials, some very-fast diffusing defects can be generated. The first-principles MD simulations done here reveal the fastest-diffusing defect we know of. This could not only explain why the isolated self-interstitial has never been observed in Si, and opens a new way of thinking about the formation and/or dissolution of self-interstitial {113} 'rods'.

3. Interstitial H_2 molecules can be an important reservoir of hydrogen in the material. However, I doubt that high concentration of this defect can survive in rather defective poly-Si material such as EFG, ribbon or others. We did show as part of an earlier NREL contract that these molecules readily dissociate when near native defects. However, the challenge here was to understand the observed strange behavior of this species, and theory has been helpful in this regard.

4. The development of first-principles theory to allow the calculation of complete dynamical matrices for an entire supercell without physically displacing any atom is a very important development. Indeed, we now can predict the most accurate local vibrational modes available to date, and this will help identify infra-red absorption lines and will speed up the (microscopic) experimental work under way elsewhere. Further, the knowledge of all the normal modes in the cell may allow us to calculate the energy of defects as a function of temperature, from first-principles. Other useful developments are under way.

5. We have performed the most complete (to date) study of the fundamental interactions for a transition metal impurity (copper) in Si. The interactions of Cu with the vacancy and the self-interstitial, with hydrogen, with oxygen, and with itself includes native defects as well as three of the most common impurities in PV material. One disappointment is that hydrogen readily binds to the transition metal, but does not passivate it.

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Thesis, talks, and publications

The contract has involved several students at Texas Tech University and resulted in a number of talks and publications. The details are listed below.

a) Dissertation and thesis

Maen Gharaibeh, *Ph.D. Dissertation*: 'Molecular-Dynamics Simulations of Self-Interstitials in Silicon' (2002)

Damien West, *M.S. Thesis:* 'Copper in Silicon' (May, 2003)

b) Invited conference talks

S.K. Estreicher: **1st International Workshop on Hydrogen in Materials and Vacuum Systems** (Jefferson Lab, Newport News, VA, 10/02): *Dynamics of hydrogen in semiconductors*

S.K. Estreicher: **12th Workshop on Crystalline Si Solar Cell Materials and Processes** (Breckenridge, 2002): *Microscopic properties of copper in silicon: theoretical predictions*

S.K. Estreicher: **31st Int. School on the Physics of Semiconductor Compounds** (Jaszowiec, Poland, 6/02): *Hydrogen molecules in semiconductors: an angel in GaAs, a devil in Si*

S.K. Estreicher: **1st Workshop on defects in Si and SiGe** (Manchester, UK, 10/01): *Dynamics of copper in Si*

S.K. Estreicher: **9th GADEST Conference** (Catania, Italy, 10/01): *Cu-defect and Cu-impurity interactions in Si*

S.K. Estreicher: **21st International Conference on Defects in Semiconductors** (Giessen, Germany, 7/01): *The fascinating dynamics of defects in silicon*

S.K. Estreicher: **Gordon Research Conf. '**Materials Processes Far From Equilibrium' (Meriden, NH 2001): *Hydrogen-Defect Interactions in Silicon*

S.K. Estreicher: **March Meeting of the American Physical Society** (Seattle, 3/01): *Molecular-dynamics studies of hydrogen-defect interactions in Si*

S.K. Estreicher: **10th NREL Workshop on Crystalline Silicon Solar Cell Materials and Processes** (Copper Mountain, CO, 8/00): *Hydrogen, passivation and related issues*

c) Technical seminars

University of Texas at Arlington (2/2000)
University of Zürich, Zürich –Switzerland (5/2000)
Max-Planck Institute f. Mikrostructurphysik, Halle-Germany (6/2000)
Technical University, Dresden-Germany (6/2000)
University of California Berkeley, CA: departmental colloquium and two seminars (10/2000)

University of Exeter, Exeter-UK (6/2001)
King's College and University College (joint seminar), London-UK (6/2001)
University of Aarhus, Aarhus-Denmark (8/2001)
Fritz-Haber Institute, Berlin-Germany (10/2001)
Technical University, Berlin-Germany (10/2001)
Max-Planck Institute f. Mikrostructurphysik, Halle-Germany (11/2001)
Walter-Schottky Seminar, Technical University, Munich-Germany (11/2001)
Centre National de Recherches Scientifiques, Strasbourg-France (11/2001)
Forschungszentrum Rossendorf , Rossendorf-Germany (11/2001)
University of Konstanz, Konstanz-Germany (12/2001)

Texas Tech University (1/2002)
Lehigh University, Bethlehem, PA (3/2002)
University of California Berkeley, CA (4/2002)
University of Milano-Bicocca, Italy (5/2002)
Max-Planck Institute f. Mikrostructurphysik, Halle-Germany (6/2002)

d) Book chapters

S.K. Estreicher: *First-Principles Theory of Copper in Silicon,* in
Copper in Semiconductors, ed. M.O. Aboelfotoh and A. Mesli (Springer-Verlag, in print)

S.K. Estreicher: *Structure and Dynamics of Point Defects in Crystalline Silicon*, in **Atomistic Modeling of Materials Properties and Phenomena**, ed. T. Frauenheim, M. Pederson, and P. Deak (Wiley-VCH, Berlin), **Physica Status Solidi (b) 217**, 513-532 (2000)

e) Invited papers

S.K. Estreicher and D. West: *Microscopic Properties of Copper in Silicon: Theoretical Predictions,*
12th Workshop on c-Si Solar Cell Materials and Processes,
NREL/BK 520-32717, 147-154 (2002).

S.K. Estreicher: *The H_2 Molecule in Semiconductors: an Angel in GaAs, a Devil in Si*,
31st International School on the Physics of Semiconductor Compounds,
Acta Physica Polonica A 102, 403-418 (2002).

S.K. Estreicher, P.A. Fedders, and P. Ordejón: *The Fascinating Dynamics of Defects in Silicon,*
21st International Conference on Defects in Semiconductors,
Physica B 308-310, 1-7 (2001)

S.K. Estreicher, D. West, and P. Ordejón: *Copper-Defect and Copper-Impurity Interactions in Silicon*,
9th GADEST Conference,
Solid State Phenomena 82-84, 341-348 (2002)

S.K. Estreicher: *Hydrogen, passivation, and related issues,*
10th Workshop on c-Si Solar Cell Materials and Processes,
NREL/BK 520-28844, 84-91 (2000)

f) Papers in refereed journals

D. West, S.K. Estreicher, S. Knack, and J. Weber: *Copper interactions with H, O, and the self-interstitial in Si,*
Physical Review B, (submitted)

S.K. Estreicher, D. West, J. Goss, S. Knack, and J. Weber: *First-principles calculations of pseudolocal vibrational modes: the case of Cu and Cu pairs in Si,*
Physical Review Letters 90, 035504 (2003)

J. Pruneda, S.K. Estreicher, J. Junquera, J. Ferrer, P. Ordejón: *Vibrational frequencies of light impurities in Si,*
Physical Review B 65, 075210/1-8 (2002)

M. Gharaibeh, S.K. Estreicher, P.A. Fedders, and P. Ordejón: *Self-interstitial-hydrogen complexes in Si,*
Physical Review B 64, 235211/1-7 (2001)

J.E. Lowther, S.K. Estreicher and H. Temkin: *Nitrogen-related complexes in GaAs*,
Applied Physics Letters 79, 200-202 (2001)

S.K. Estreicher, K. Wells, P.A. Fedders, and P. Ordejón: *Dynamics of hydrogen molecules in silicon,*
Journal of Physics: Condensed Matter 13, 62-71 (2001)

S.K. Estreicher, M. Gharaibeh, P. Fedders, P. Ordejón: *Unexpected dynamics for self-interstitial clusters in Si,*
Physical Review Letters 86, 1247-1250 (2001)

J.R. Byberg, B. Bech Nielsen, M. Fanciulli, S.K. Estreicher, and P.A. Fedders: *Dimer of substitutional carbon in silicon studied by EPR and ab-initio methods,*
Physical Review B 61, 12939-12945 (2000)

B. Hourahine, R. Jones, A.N. Safonov, S. Öberg, P.R. Briddon, and S.K. Estreicher: *Identification of the Hexavacancy in Silicon with the* B^4_{80} *Optical Center,*
Physical Review B 61, 12594-12597 (2000)

g) <u>Contributed papers</u>

M. Stavola, F. Jiang, S.K. Estreicher, J.L. McAfee, A. Rohatgi, D. Kim, J. Holt, H. Atwater, and J. Kalejs, *Hydrogenation of bulk Si from* SiN_x*:H films: what really ends up in the Si?*
Proc. 2003 NREL Solar Pgm Review Meeting (Denver, CO), ed. S. Asher

McAfee and S.K. Estreicher: *Isolated N and N pairs in silicon,*
12th Workshop on Crystalline Silicon Solar Cell Materials and Processes (Breckenridge, CO 8/02),
NREL/BK 520-32717, 171-174 (2002)

S.K. Estreicher, D. West, J.M. Pruneda, S. Knack, and J. Weber: *Formation and properties of three copper pairs in silicon,*
Materials Research Society Symposium Proceedings 719, 421-426 (2002)

S. Knack, J. Weber, and S.K. Estreicher: *Defect reactions of copper in silicon,*
ElectroChemical Society Proceedings in print (2002)

J.M. Pruneda, J. Junquera, J. Ferrer, P. Ordejón, and S.K. Estreicher: *Vibrational Properties of H-related defects in Si,*
Physica B 308-310, 147-150 (2001)

S.K. Estreicher, J.L. McAfee, P.A. Fedders, J.M. Pruneda, and P. Ordejón: *The strange behavior of interstitial* H_2 *molecules in Si and GaAs,*
Physica B 308-310, 202-205 (2001)

M. Gharaibeh, S.K. Estreicher, P.A. Fedders: *Dynamics of self-interstitials precipitation using the* I_3 *cluster,*
Physica B 308-310, 510-512 (2001)

S.K. Estreicher: *Theory of defects in semiconductors*
High Performance Computing Center Newsletter, Feb. 2001

M. Gharaibeh, S.K. Estreicher, and P.A. Fedders: *Molecular dynamics for self-interstitials in Si*,
10th Workshop on Crystalline Si Solar Cell Materials and Processes (Copper Mountain, CO 8/00),
NREL/BK 520-28844, 129-132 (2000)

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13. ABSTRACT *(Maximum 200 words):* The objective of the research under this contract is to perform systematic first-principles calculations on native defects and selected transition metal impurities in Si and their interactions with hydrogen. One goal is to gain insight into which defects need to be passivated and which ones do not, which defects are the most stable, and how interactions with H affect their electrical and optical properties. This work includes potential surface and electronic structure calculations, as well as real-time, constant-temperature, molecular dynamic simulations to test the thermal stability of various defects and monitor defect reactions and/or diffusion. Another goal is to predict the local vibrational modes, the binding and various activation energies of the most important H complexes, and other quantities that have been or can be measured experimentally. Further, theory itself needs to be continuously developed to allow more accurate predictions and the calculation of quantities that are beyond the reach of today's "state-of-the-art." The following issues are discussed in this report.

14. SUBJECT TERMS: PV; molecular dynamic (MD); manufacturer; density-functional (DF); hydrogen; local vibrational modes (LVMs); transition metal; first-principles calculations; native defects; hydrogen; passivation; silicon; thermal stability; binding energy; activation energy; H complexes	15. NUMBER OF PAGES 16. PRICE CODE

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