PHYSICAL REVIEW B VOLUME 45, NUMBER 23 15 JUNE 1992-I

Titanium and copper in Si: Barriers for diffusion and interactions with hydrogen

David E. Woon and Dennis S. Marynick
Department of Chemistry, The University of Texas at Arlington, Arlington, Texas 76019-0065

Stefan K. Estreicher
Department of Physics, Texas Tech University, Lubbock, Texas 79409-1051

(Received 23 September 1991)

We present the results of a theoretical study of the diffusion barriers of titanium and copper in crystalline silicon, and of the interactions between titanium and hydrogen, and between copper and hydrogen. The calculations were performed using various molecular clusters and the Hartree-Fock method. The method of partial retention of diatomic differential overlap (PRDDO) predicts diffusion barriers of 3.29 eV for Ti^+, 2.25 eV for Ti^0, and 0.24 eV for Cu^+. PRDDO also predicts that substitutional Ti^0 is a deep trap for interstitial H, with a gain in energy of 1.84 eV relative to atomic H far outside the cluster. *Ab initio* Hartree-Fock calculations show that a Ti^+ ion at a tetrahedral interstitial site also forms a bond with interstitial H, with a dissociation energy of 2.31 eV. On the other hand, interstitial Cu^+ does not form a bond with H. Several issues relevant to H passivation of interstitial 3*d* transition metal-impurities in Si are discussed.

I. INTRODUCTION AND BACKGROUND

The presence of transition metal (TM) impurities[1-3] in doped and undoped silicon semiconductor material causes significant changes in the electronic properties of devices. Most TM's create deep levels in the band gap that considerably reduce the lifetime and mean free path of charge carriers. This is clearly desirable in the case of fast switches, in which gold and other impurities are used for this purpose. On the other hand, the efficiency of photovoltaic devices suffers greatly from the presence of such impurities. While gettering is an efficient way of controlling the concentration of some TM impurities (Au, for example), it is mostly ineffective in the case of slowly diffusing ones such as V or Ti. These impurities are introduced during growth or processing, and remain essentially immobile in the Si lattice.

The effect of TM impurities[1,2] varies greatly from one side of the TM block in the Periodic Table to the other. Even in concentrations lower than 10^{14} cm^{-3}, Ti can reduce the efficiency of some solar cells by as much as 50% making it one of the worst offenders. It also exhibits two other undesirable properties: it is an excessively slowly diffusing species, which makes it extremely difficult to remove with standard gettering techniques.[4] Further, hydrogen, which easily passivates[1] Au, appears to have no passivating effect[5] on the deep levels of Ti. Copper, at the other extreme, diffuses rapidly through the Si lattice, much faster than hydrogen in fact, and creates no deep levels when isolated.

To date, theoretical efforts[6-8] aimed at understanding the properties of TM impurities in Si have been restricted to studies of their electronic structures. Except for an elastic-energy approach by Utzig,[9] neither potential energy surfaces nor interactions with other interstitials have been investigated. In the present work, we focus not on the electronic structures, which are now well understood, but rather on diffusion barriers and interactions with interstitial H. Our calculations confirm the high barrier for titanium and the much lower barrier for copper. Furthermore, we show that substitutional Ti^0 and interstitial Ti^+ form strong bonds with H, while interstitial Cu^+ does not.[10]

Titanium has been observed via electron paramagnetic resonance[11] and electron-nuclear double resonance[12] at an interstitial site in the +1 charge state, with three 3*d* electrons filling half of a t_2 level to form a quartet $^4A_2$ state. Although no experimental observation of substitutional Ti^0 has been reported, the presence of four 3*d* electrons suggests that there may be some tendency for it to choose a substitutional site, were such a site available (this has been noted by Weber[3]). Estimates of the diffusion barrier for Ti have crept towards higher values over the years, from 1.50 (Ref. 13), to 1.66 (Ref. 4), to 1.79 eV (Ref. 14), and, more recently, to 2.05 eV (Ref. 15).

Copper is normally found as Cu^+ in Si, where the $3d^{10}$ configuration is decidedly stable. As a small, closed-shell ion, Cu^+ has little tendency to interact with the lattice. However, it does passivate[16,17] shallow acceptors, and forms complexes with lattice defects.[16,18] Experimental estimates of its diffusion barrier range from 0.43 eV (Ref. 19) to 0.15 eV (Ref. 20).

Our primary purpose in this work is to begin to address some of the fundamental questions about the interactions of TM impurities with interstitial H in Si. It would seem advantageous to start this process by comparing two very different impurities: Ti, which is immobile and electrically very active, and Cu, which diffuses rapidly and, by itself, is largely inactive. The most pointed questions are these: Why does hydrogen not passivate the deep levels of titanium? Can hydrogen even bind to titanium? How do copper and hydrogen interact? What constitutes passivation, and what criteria are appropriate for distinguishing a passivated state from a nonpassivated one in the context of a computational simulation?

Our results (Sec. III) show that H forms a bond with both substitutional Ti^0 and interstitial Ti^+, provided that titanium and hydrogen are able to reach their respective bonding locations. On the other hand, interstitial Cu^+ does *not* form a bond with H. Interstitial Cu^0 does form a hydride in Si, but the Cu-H bond is quite weak indicating an unstable interaction.

At this early stage in the study of TM interactions with other impurities in Si, we are unable to confirm the experimental observation that H does not passivate Ti. We will, however, utilize our current body of results to propose (Sec. IV) several possible explanations and make recommendations for future work using both computational and experimental approaches.

II. METHODOLOGY

Our primary methodology is the nonempirical PRDDO (partial retention of diatomic differential overlap) method developed by Halgren and Lipscomb,[21] and expanded by Marynick and Lipscomb[22] to include the first period of TM's. The PRDDO method makes approximations which reduce the cost of calculating two electron integrals. Whereas *ab initio* methods scale as $N^4/8$, where N is the number of basis functions, PRDDO scales as N^3. The method expands the molecular states over a basis set of optimally orthogonalized atomic orbitals constructed from a minimum basis set of Slater-type orbitals (STO's). PRDDO has been rather successful at predicting geometries and relative energies.[23] We have also made use of the GAMESS (Ref. 24) implementation of unrestricted *ab initio* Hartree-Fock (UHF) theory.[25]

Clusters of various sizes and characteristics were used to represent the Si crystalline environment. The dangling bonds on the cluster surfaces were saturated with H atoms.[26] In the diffusion studies, three clusters were utilized: $Si_{10}H_{16}$ (labeled "T2" in this paper), $Si_{14}H_{20}$ (or "THT"), and $Si_{30}H_{40}$ (or "T4"). The first and last of these clusters are centered at a tetrahedral interstitial (T) site and have two and four shells of Si atoms around the T site, respectively. The THT cluster is centered at a hexagonal (H) site and is flanked by two symmetrically located T sites. For substitutional Ti^0 with H, we used $Si_{14}H_{24}$ (or "BC-AB") and $Si_{35}H_{36}$ (or "$S4$") clusters. The former is the smallest cluster which provides reasonable environments for both an antibonding (AB) and a bond-centered (BC) site. The latter cluster consists of four shells around a substitutional (S) site. To investigate the interactions between interstitial Ti^+ and H, we used the THT cluster described above. In the Cu and H case, the THT and T4 clusters were used.

III. RESULTS

A. Diffusion barriers for Ti^0, Ti^+, and Cu^+

Diffusion barriers for the (spin) triplet Ti^0, the quartet Ti^+, and the singlet Cu^+ were calculated using PRDDO and the three clusters detailed above. The barrier energy was taken to be the difference in energy between the clusters with the impurity at the H and at the T sites. The H site was explicitly demonstrated to be the saddle point. For Ti^0 and Ti^+ in the T4 cluster, a number of host atoms around the H or T site were allowed to relax. At the T site, the four nearest neighbors (NN's) and the six next-nearest neighbors (NNN's) were allowed to breathe radially. At the H site the six NN's were allowed to relax radially, and the angle formed by each of the six Si atoms with the Ti and the THT axis was also relaxed. No relaxation was considered in the case of Cu^+ due to its small calculated barrier for diffusion.

The barrier heights are given in Table I. Lattice relaxation makes a very important contribution to reducing the size of the barriers. Our most reliable values are 3.29 eV for Ti^+, 2.25 eV for Ti^0, and 0.24 eV for Cu^+. Although Ti^+ is considered to be the more stable species, we observe that Ti^0 has a significantly lower barrier for diffusion, closer to the high end of the experimental values.[15] The barrier for Ti^0 is more than 1 eV lower than that of Ti^+. A charge-state-dependent diffusion barrier has recently been reported[27] in the case of interstitial Fe, the barrier being higher for Fe^0 than for Fe^+.

The low barrier for Cu^+ diffusion is consistent with the idea that its filled $3d$ shell does not interact to any great extent with the lattice. The barrier height is largely predicated upon the actual size of the ion (which is small) and, to a much lesser extent, by the polarization effects caused by the +1 charge.

On the other hand, Ti^0 and Ti^+ each have unpaired electrons which create appreciable interactions with the lattice. A quantitative measure of the strength of these interactions is the degree of bonding,[28] which has a value of exactly 1 for a perfect two-electron covalent bond, such as Si-Si in the perfect lattice. At the T site, the degrees of bonding of Ti^+ to its 4 NN and 6 NNN Si centers are 0.54 and 0.33, respectively. At the H site, the degree of bonding of Ti^+ to each of its 6 NN's is 0.61. The numbers for Ti^0 are almost identical. Much of the charge density needed to form these weak but numerous bonds between Ti and the host lattice comes at the cost of weakening the Si_{NN}-Si_{NNN} bonds, which have much smaller degrees of bonding when Ti is present than when it is not.

The small differences in the degrees of bonding between

TABLE I. Diffusion barriers for Ti^0, Ti^+, and Cu^+ in Si calculated with PRDDO. Our best estimates of the barrier heights are in bold print.

Species	State	Cluster	Relaxed	Barrier (eV)
Ti^+	Quartet	T2	No	5.75
		THT	No	5.16
		T4	No	5.68
		T4	**Yes**	**3.29**
Ti^0	Triplet	THT	No	3.75
		T4	**Yes**	**2.25**
Cu^+	Singlet	T2	No	0.17
		THT	No	0.30
		T4	**No**	**0.24**

Ti^+ and Ti^0 and the lattice are too small to account for the 1.04 eV difference between their respective diffusion barriers. In seeking an explanation for this behavior, we have investigated spin delocalization effects as well as group theoretical differences.

An analysis of the atomic spin population for the Ti species and its Si_{NN}'s and Si_{NNN}'s indicates a preferential delocalization in the case of Ti^0 at the H site (see Table II). The total Si spin population gives a measure of the degree to which the unpaired electrons from Ti are delocalized. The values for Ti^0 and Ti^+ differ substantially at the H site, where much of the spin density of Ti^0 is shifted to its Si_{NN}'s. In the case of Ti^0, this delocalization *appears* to stabilize the H site. However, the interpretation of *spin* delocalization is not as straightforward as that of *electron* delocalization. Indeed, electron delocalization should be accompanied by a lengthening of the Si_{NN}-Si_{NNN} bonds and a lowering of the corresponding degrees of bonding, which we do not observe here. This is because the only orbitals capable of accepting electrons from Ti are Si-Si orbitals which are antibonding in character. Populating these orbitals must result in a weakening of the bonding interactions. Thus, the spin delocalization which occurs here is not necessarily the reason for the difference in barrier heights.

A more likely explanation can be obtained from group theory, specifically the way the d electrons from the triplet Ti^0 and the quartet Ti^+ are occupied in the crystalline environment. At the T site, which has T_d symmetry, all the electrons are found in a single state, t_2, which lies below an unoccupied e_g state. At the H site, with D_{3h} symmetry, the d orbitals split into three levels: an a_{1g} state [formed from the $z^2 - (x^2 + y^2)/2$ Ti orbital] which can hold two electrons, and two e_g states (the lower one from zx and yz, the higher one from $x^2 - y^2$ and xy) which can hold four electrons each. At the H site, the orbital population for Ti^+ indicates that there is one spin-up electron in the a_{1g} state, and two spin-up electrons in the lower e_g state. In the case of Ti^0, the fourth electron is spin-down and completes the pair in the a_{1g} state.

The result of this distribution is that the population of Ti^+ is much closer to spherical than that of Ti^0, where more electrons are in the d orbitals oriented along the z direction, which is the direction of the T-H-T axis. At the H site, Ti^0 is much more elongated than Ti^+, and thus "squeezes" more easily through the lattice than Ti^+, which looks much more spherical. The total density in the zx plane for Ti^0 and Ti^+ at the H site is shown in Fig. 1.

TABLE II. Spin populations for Ti^+ and Ti^0 in the T4 cluster. At the T site, the Si values are the sum of the individual values for the 4 NN and the 6 NNN Si atoms to Ti. At the H site, they are the sum of the 6 NN's. The amount of spin delocalization is indicated: A value of 0% means that all the spin is localized on Ti, and a value of 100% corresponds to complete delocalization.

		Net spin population			
Species	Center(s)	T site	% deloc.	H site	% deloc.
Ti^+	Ti	2.788	7.1%	2.555	17.4%
	Si	0.232		0.318	
Ti^0	Ti	1.774	11.3%	1.197	**40.2%**
	Si	0.244		0.780	

B. Interactions of substitutional Ti^0 with H

Ti^0 with its $3d^4$ outer shell configuration might well be expected to be present in Si as a substitutional impurity. This should not be an electrically active impurity, simply because there are four electrons which all have well-defined roles to follow in bonding.

Using PRDDO exclusively, we performed one optimization cycle in the small AB-BC cluster with hydrogen near the BC site and at the AB location. Three centers were adjusted: Ti^0, H, and the Si_{NN} atom lying along the trigonal axis. The resulting geometry was then used as an input for further optimizations in the larger $S4$ cluster. We also calculated a reference energy, corresponding to the cluster with substitutional Ti plus H far outside the cluster. Computationally, this was done by calculating the energies of $TiSi_{34}H_{36}$ and H separately, and adding the numbers.

Figure 2 shows substitutional Ti^0 with H at the BC site and at the AB site. The BC case exhibits a net gain in

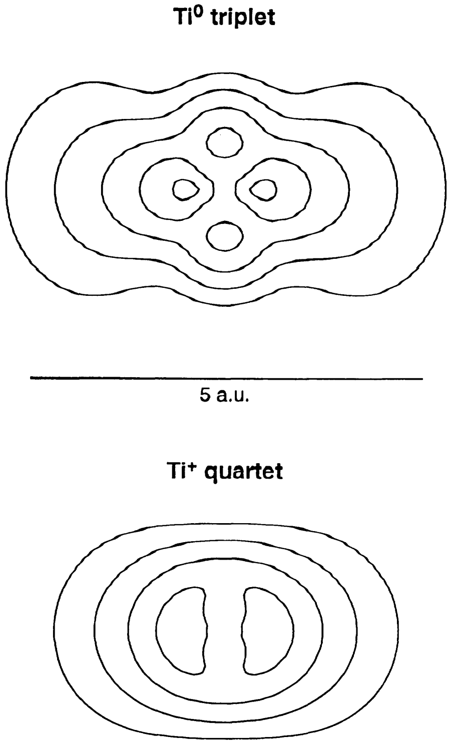

FIG. 1. Section through the zx plane (the z axis is the T-H-T direction) of the total electronic density for the triplet Ti^0 and the quartet Ti^+ at the H site in Si. The outermost contour corresponds to 0.03 a.u., and each successive contour is a factor of 2 higher. Because of the way the a_{1g} and e_g states are populated, Ti^0 has a much more elongated shape than Ti^+, and its barrier for diffusion is much lower.

energy of −1.84 eV relative to H outside the cluster, while H at the AB site is bound with −0.47 eV only. The latter configuration may or may not be metastable in reality, i.e., calculations in larger clusters with larger basis sets would be needed to confirm that this is a true local minimum rather than a saddle point of the energy. However, the BC case is the typical sort of bonding realized[29,30] for hydrogen in Si. It should be noted that when H is at a BC site in perfect Si, and at the same level of theory, it *costs* 0.25 eV to put it there starting from atomic H far outside the cluster.[31] This shows that substitutional Ti^0 is indeed a very strong trap for interstitial H.

C. Interactions of interstitial Ti^+ with H

We approached this problem with the *ab initio* UHF methodology and the THT cluster. Minimal basis sets[32] were used for Si and H. The basis set for Ti was adapted from functions determined by Hansen and Marynick.[33]

Initially, interstitial H was restricted to motion along the C_3 axis (the $<111>$ crystallographic direction) which connects the two T sites via the H site. The Ti^+ was left at the T site throughout. A net triplet state was formed by combining the three spin-up Ti^+ electrons with a spin-down H electron. The quintet state (with a spin-up electron contributed by H) was also calculated for several points and found, as expected, to result in a repulsive interaction. The quintet was also used subsequently to compare the large-separation behavior of the quintet and triplet states.

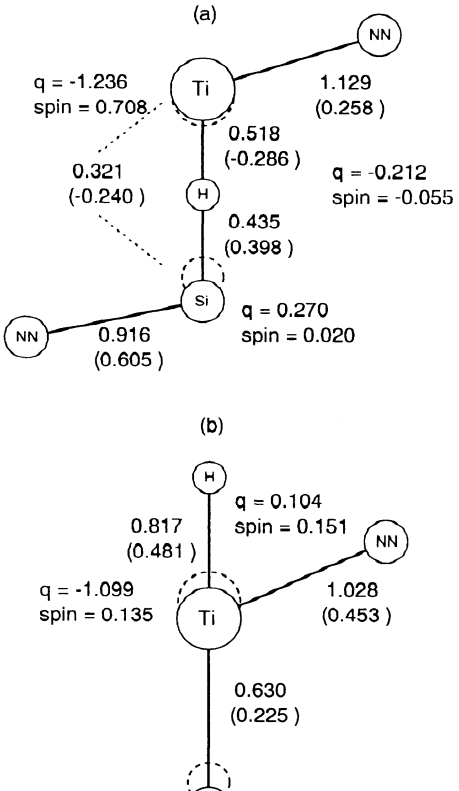

FIG. 2. Substitutional Ti^0 with interstitial H. (a) H near the BC site (Ti-H=1.28 Å, Si-H=1.46 Å). (b) H at the AB site (Ti-H=1.61 Å, Ti-Si=2.47 Å). q is the (Mulliken) charge, "spin" is the atomic spin population, and the pairs of numbers are the degrees of bonding (Ref. 28) (upper number) and the overlap population (lower number in parentheses). Configuration (a) is 1.37 eV lower than configuration (b).

Figure 3 shows the potential energy surface for the H atom as noted above. The minimum occurs for a Ti-H separation of 1.66 Å. There is a shoulder near the T site which is the remnant of the energy minimum that H would experience without the presence of the Ti^+ ion. The dashed line is an approximation of the diffusion path[29] of H without Ti^+. From this, we obtain a first estimate of at least 2.20 eV for the dissociation energy of the Ti^+-H bond in Si.

In a UHF calculation, the spin-up and spin-down orbitals are optimized separately. As a result, the expectation value $< S^2 >$ usually exceeds somewhat $s(s+1)$, and the wave function is not an exact eigenfunction of S^2, although it is an eigenfunction of S_z. The difference $< S^2 > -s(s+1)$ is called "spin contamination." In most situations, it is small and UHF results are in good agreement with those obtained using much more expensive wave functions, such as restricted open-shell Hartree-Fock, which are true eigenfunctions of S_z and S^2. However, a large spin contamination may reflect a dubious value of the total energy.

In our case the contamination in the vicinity of the minimum is slight: 2.07 versus an uncontaminated value of 2.00. At the minimum, the wave function is very close

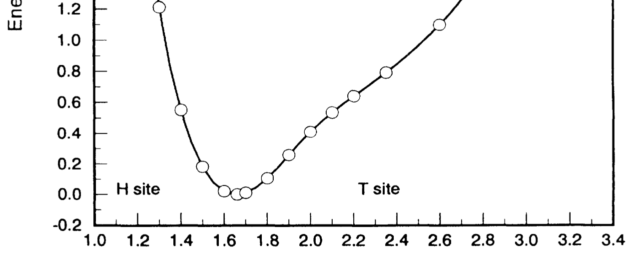

FIG. 3. Potential energy surface for H displaced along the T-H-T axis towards interstitial Ti^+ (solid line) and estimated surface for H diffusion *without* Ti^+ (broken line). The H site is at 1.176 Å, and the T sites are at 0 (location of Ti^+) and 2.352 Å.

to an exact triplet, as would be found in a more rigorous multideterminant calculation. As the separation between Ti and H increases, the contamination quickly balloons (reaching 2.87 at 2.35 Å) as the individual identities of the two species begin to emerge. In order to estimate the reliability of our energetics in this situation, we checked the value of the energy of the separated Ti^+ and H species by comparing the asymptotic values for both the triplet and quintet spin states. At large distances, the two configurations should become degenerate, and this is indeed what happens. For the Ti^+-H separation of 3.3 Å, the energy splitting between the two spin states is only 0.02 eV, in spite of the large spin contamination. This is a strong indication that the dissociation energy is a much better value than the amount of spin contamination might at first suggest.

The same spin contamination behavior is observed when the H atom is moved off the $<111>$ direction along another trigonal axis. At a further H site, although the triplet state is contaminated, the triplet-quintet energy difference is only 0.07 eV. Thus, the energy difference between the minimum in Fig. 3 and the adjacent H site is 2.20 eV, with an uncertainty of the order of 0.07 eV (2.20 eV is a lower limit).

To get an even better estimate of the bond energy, we repeated the previous set of calculations in a cluster where the ten Si atoms near the Ti^+ ion were allowed to relax. The relaxed separations were found in the course of determining the diffusion barrier for Ti^+ (see above). The NN distance was found to increase from 2.352 to 2.421 Å, and that of the NNN from 2.715 to 2.784 Å. All the relaxations were performed by moving radially outward from the Ti^+ center. The equilibrium Ti^+-H bond length decreases very slightly to 1.65 Å. The dissociation energy of the Ti^+-H bond increases after relaxation to 2.31 eV, with the triplet-quintet energy difference at 0.06 eV.

In both the relaxed and the unrelaxed cases, there is significant overlap between Ti^+ and H. Upon bonding, the t_2 state of Ti^+ splits into e (two spin-up electrons) and a (one spin-up electron) states. The electron from H ends up largely in the a state as the spin-down member. At the relaxed minimum, the e states have energies of -0.412 a.u., the a spin-up state lies at -0.381 a.u. and the down-spin state at -0.388 a.u. The smallness of this discrepancy is another indication of the high purity of the triplet state. The Ti^+ t_2 state (with no H in the neighborhood) has an energy of -0.400 a.u.

Pearton, Corbett, and Shi[34] have compiled a table of estimates of dissociation energies of hydrogen from a number of deep level impurities. Our values lie within their range of 1.5–2.5 eV.

D. Interactions of interstitial Cu with H

The interactions between interstitial Cu and interstitial H were obtained in the T4 cluster after performing preliminary runs in the smaller THT cluster. Cu was first placed at a T site and H was allowed to move from the nearest T site towards Cu, towards other sites in the cluster, and, in the case of Cu^+, to "infinity" (far outside the cluster). In order to investigate the behavior of the {Cu,H} pair, both atoms were allowed to move.

Cu^+ does not form a bond with H in Si. In the lowest-energy configuration, both atoms remain fairly close to their respective T sites. After optimization, the Cu^+-H separation is 2.193 Å and the degree of bonding is 0.05, which is effectively zero. The copper ion overlaps with its Si NN's and NNN's, but not with H. Further, it *costs* 1.55 eV to take H far outside the cluster and place it at the most favorable site near Cu^+. This is 0.35 eV *more* energy[30] than is required to place H at a T site without Cu^+ in its vicinity. This is a clear indication that the H-Cu^+ interaction is repulsive.

For completeness, we also checked the possibility that Cu^0 might form a bond with H. In this case, geometry optimizations show that Cu^0 moves away from the T site towards H and does indeed form a covalent bond with it. Cu^0 moves along the trigonal axis, away from one of its Si NN's, and reduces its overlap with this atom. Cu^0 ends up almost at the H site, while H remains very close to its T site. The Cu-H bond is poorly formed. The degree of bonding is 0.69, which is substantially less than a two-electron covalent bond.

IV. DISCUSSION

We have studied the diffusion barriers of interstitial Ti and Cu in crystalline Si, their interactions with H, and the interactions between substitutional Ti^0 and H. All the calculations used minimal basis sets with fixed contracted double-zeta $3d$ orbitals on Ti. The barriers for diffusion of the interstitials were obtained using the method of PRDDO to allow the study of cluster size effects. These effects are small, as indicated in Table I (compare the unrelaxed barriers). Further, we investigated lattice relaxation effects (first and second NN's) around Ti, and found these effects to be large. The interactions between substitutional Ti^0 and H were obtained at the *ab initio* UHF level.

The calculated barriers for diffusion reflect the trends observed experimentally, with a very low barrier for Cu^+ (0.24 eV) and very high barriers for Ti^0 (2.25 eV) and Ti^+ (3.29 eV). The large difference between the barriers for the triplet Ti^0 and the quartet Ti^+ are explained by the difference in shape of these species at the H site (Ti^+ is almost spherical while Ti^0 is much more elongated) which in turn is caused by the way the $3d$ orbitals of Ti are populated along the z direction. In addition, the spin density of Ti^0 is much more delocalized at the H site than that of Ti^+.

Our calculations show that interstitial Cu^+ does not form a bond with H and that the two species tend to avoid each other in the perfect lattice. Of course, this does not imply that both impurities cannot be found interacting with a defect. On the other hand, Cu^0 forms a hydride in Si, but the Cu-H bond is weak.

Substitutional Ti^0 is a strong trap for H, which bridges one of the four Ti-Si bonds. Hydrogen is more stable there by 1.84 eV than far outside the cluster containing substitutional Ti^0. This center is not expected to be electrically active.

The interactions between H and interstitial Ti^+ show that the two species form a covalent bond, provided that they can reach their respective bonding locations.

We are drawn back to the original question: Why does hydrogen not passivate interstitial titanium? The results of this work indicate that Ti^+ and H will form a strong bond. The formation of a bond seems to have been the most common computational criterion for determining whether shallow acceptors or donors (B and P in particular) are being passivated by H. This criterion may not be useful for judging the activity of TM's. It may be necessary instead to study what happens to the deep levels of Ti^+ as H atoms are added, by accurately calculating the energy levels of the various charge states for each of the general complexes $^p[(\mathrm{TM})\mathrm{H}_n]^m$, where TM is the transition-metal atom, H is hydrogen, p is the state multiplicity, n can range from 1 to 4 (there being only four T-H-T approaches), and m is the charge state.

Why consider the general complex $^p[(\mathrm{TM})\mathrm{H}_n]^m$? For substitutional B and P, the valence differs by only ±1 from that of the host Si atoms. In the case of Ti and other $3d$ TM's which tend to occupy interstitial sites, there are multiple unpaired electrons, partially filling a t_2 and/or e levels deep in the gap. It may well be that some TM's cannot be passivated unless two, three, or even four hydrogens are bound to them. Then, the appropriate strategy may no longer be to simply determine if a single H will bind to the TM, but to learn if there is a sufficient thermodynamic driving force to attract enough H interstitials to completely passivate the defect by filling up all the gap levels.

There are a large number of unknowns in the study of passivation. Although we have demonstrated that at least one H will form a strong bond with interstitial Ti^+ at a T site, this is not sufficient to passivate all the Ti deep levels. Further, it is not clear whether H can, in fact, even reach the site where the bond forms. A current theory[31] suggests that although H diffuses mostly as H^0 at low temperatures, via interstitial T-H-T paths, it spends a certain amount of time at BC sites as H^+. Could that be responsible for a long-range repulsion that simply keeps H away from Ti^+, even though the trap is *locally* deep? The two TM's to the right of Ti in the Periodic Table are V and Cr. Vanadium is not passivated, but chromium is partially passivated.[34] Vanadium has been observed as V^{2+} and chromium as both Cr^+ and Cr^0 (Ref. 35). If it is Cr^0 that is passivated while Cr^+ and V^{2+} are not, there is at least some possibility that the idea of a long-range repulsion is correct. It would be useful if experiment (such as infrared absorption) could determine whether H does or does not form bonds with any of the $3d$ TM's, independently of whether passivation occurs or not.

In the meantime, theorists can continue to investigate this question computationally. The study of the series of general TM complexes $^p[(\mathrm{TM})\mathrm{H}_n]^m$ (see above) in Si should teach us much about the nature of passivation. These investigations are quite involved, due to the complexity of the electronic structures and the large number of possible spin multiplicities for each charge state, as well as to convergence problems which often occur when dealing with TM's in general.

While many questions remain unanswered, we have demonstrated that — given the chance — interstitial titanium forms a bond with hydrogen and that this bond is strong. The energy for the interaction between substitutional Ti^0 and H at a BC site is -1.85 eV relative to H outside the cluster, and our best number for the dissociation energy of the interstitial $\{\mathrm{Ti,H}\}^+$ complex is 2.31 eV. On the other hand, interstitial Cu^+ repels H.

We have presented theoretical numbers for the interactions of Ti and Cu with hydrogen in Si, and for the diffusion barriers of Ti^0, Ti^+, and Cu^+.

ACKNOWLEDGMENTS

This research was supported in part by the Grants Nos. Y-743 (to D.S.M.) and D-1126 (to S.K.E.) from the Robert A. Welch Foundation, and a grant from the Advanced Technology Program of the State of Texas. Some computational resources were provided by the University of Texas Center for High Performance Computing.

---

[1] S. J. Pearton, in *Hydrogen in Semiconductors*, edited by J. I. Pankove and N. M. Johnson (Academic, San Diego, 1991), Chap. 5.

[2] A. Zunger, Solid State Phys. **39**, 275 (1986).

[3] E. R. Weber, Appl. Phys. A **30**, 1 (1983).

[4] K. Leo, R. Schindler, J. Knobloch, and B. Voss, J. Appl. Phys. **62**, 3472 (1987).

[5] R. Singh, S. J. Fonash, and A. Rohatgi, Appl. Phys. Lett. **49**, 800 (1986).

[6] G. G. DeLeo, G. D. Watkins, and W. B. Fowler, Phys. Rev. B **23**, 1851 (1981); **25**, 4962 (1982); **25**, 4972 (1982); Physica **116B**, 28 (1983).

[7] A. Zunger and U. Lindefelt, Phys. Rev. B **26**, 5989 (1982); **27**, 1191 (1983); A. Zunger, *ibid.* **28**, 3628 (1983); H. Katayama-Yoshida and A. Zunger, Phys. Rev. Lett. **53**, 1256 (1984); Phys. Rev. B **31**, 7877 (1985).

[8] F. Beeler, O. K. Anderson, and M. Scheffler, Phys. Rev. Lett. **55**, 1498 (1985); Phys. Rev. B **41**, 1603 (1990).

[9] J. Utzig, J. Appl. Phys. **65**, 3868 (1989).

[10] Notation: The charge states of Ti and Cu will, in general, be given explicitly. No explicit charge (as in the previous sentence) indicates a general reference to the element and its ions. Atomic hydrogen and crystalline silicon will be denoted simply as H and Si.

[11] D. A. van Wezep and C. A. J. Ammerlaan, J. Electron. Mater. **14a**, 863 (1985).

[12] D. A. van Wezep and C. A. J. Ammerlaan, Phys. Rev. B **32**, 7129 (1985); **37**, 7268 (1988).

[13] V. P. Boldyrev, I. I. Pokrovskii, S. G. Romanovskaya, A. V. Tkach, and I. E. Shimanovich, Fiz. Tekh. Poluprovodn. **11**, 1199 (1977) [Sov. Phys. Semicond. **11**, 709 (1977)].

[14] S. Hocine and D. Mathiot, Mater. Sci. Forum **38-41**, 725 (1989).

[15] H. Nakashima and K. Hashimoto, Mater. Sci. Forum **83-87**,

227 (1992).

[16] T. H. Prescha, T. Zundel, J. Weber, H. Progge, and P. Gerlach, Mat. Sci. Eng. B **4**, 79 (1989); B. G. Svensson and M. O. Aboelfotoh, Mater. Sci. Forum **65-66**, 253 (1990); R. Keller, M. Deicher, W. Pfeiffer, H. Skudlik, D. Steiner, and Th. Wichert, Phys. Rev. Lett. **65**, 2023 (1990).

[17] S. K. Estreicher, Phys. Rev. B **41**, 5447 (1990); M. O. Aboelfotoh and B. G. Svensson, Phys. Rev. B **44**, 12 742 (1991).

[18] B. G. Svensson and M. O. Aboelfotoh, Mater. Sci. Forum **83-87**, 179 (1992); A. Mesli and T. Heiser, *ibid.* **83-87**, 161 (1992).

[19] R. N. Hall and J. H. Racette, J. Appl. Phys. **35**, 379 (1964).

[20] R. Keller, M. Deicher, W. Pfeiffer, M. Skudlik, D. Steiner, and Th. Wichert, Phys. Rev. Lett. **65**, 2023 (1990).

[21] T. A. Halgren and W. N. Lipscomb, J. Chem. Phys. **58**, 1569 (1973).

[22] D. S. Marynick and W. N. Lipscomb, Proc. Natl. Acad. Sci. U.S.A. **79**, 1341 (1982).

[23] L. Throckmorton and D. S. Marynick, J. Comp. Chem. **6**, 652 (1985).

[24] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, J. H. Jensen, S. Koseki, M. S. Gordon, K. A. Nguyen, T. L. Windus, and S. T. Elbert, QCPE Bull. **10**, 52 (1990).

[25] J. A. Pople and R. K. Nesbet, J. Chem. Phys. **22**, 571 (1954).

[26] S. K. Estreicher, A. K. Ray, J. L. Fry, and D. S. Marynick, Phys. Rev. Lett. **55**, 1976 (1985); **57**, 3301 (1986); S. K. Estreicher, Phys. Rev. B **37**, 858 (1988).

[27] T. Heiser and A. Mesli, Appl. Phys. Lett. **58**, 2240 (1991).

[28] D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, J. Chem. Soc. Dalton Trans. **8**, 838 (1973).

[29] S. K. Estreicher, Phys. Rev. B **36**, 9122 (1987).

[30] S. K. Estreicher, L. Throckmorton, and D. S. Marynick, Phys. Rev. B **39**, 13 241 (1989).

[31] C. H. Chu and S. K. Estreicher, Phys. Rev. B **42**, 9486 (1990).

[32] W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys. **51**, 2657 (1969); W. J. Hehre, R. Ditchfield, and R. F. Stewart, *ibid.* **52**, 2769 (1970); M. S. Gordon, M. D. Bjorke, F. J. Marsh, and M. S. Korth, J. Am. Chem. Soc. **100**, 2670 (1978).

[33] L. M. Hansen and D. S. Marynick, J. Phys. Chem. **92**, 4588 (1988).

[34] S. J. Pearton, J. W. Corbett and T. S. Shi, Appl. Phys. A **43**, 153 (1987).

[35] As tabulated, for example, by F. Beeler, O. K. Andersen, and M. Scheffler, Phys. Rev. B **41**, 1603 (1990).