What is So Strange about Hydrogen Interactions in Germanium ?

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Qualitative differences in the behavior of H in Si and Ge have been reported. In Si, shallow acceptors and donors are easily passivated by exposure to atomic H. In Ge, only one successful attempt at acceptor passivation has been reported and donor passivation was never realized. Further, the amount of D that penetrates into a Si sample exposed to a D plasma increases with the temperature of the plasma. The opposite holds for Ge. Other qualitative differences are apparent from muon spin rotation studies. Our systematic calculations of properties of H in diamond, Si, Ge, and α-Sn show that there may be a very simple explanation for all these differences.

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The properties of hydrogen in crystalline semiconductors, mainly Si, have been studied extensively over the past ten years. Atomic hydrogen removes much of the electrical activity associated with extended defects (such as dislocations or grain boundaries), but also interacts with a wide range of point defects as well as with the host crystal itself. The results of these interactions are considerable changes in the electrical and optical properties of the crystal.

In silicon, H easily passivates acceptors and donors, partially or fully passivates double and triple acceptors and donors (including O-related thermal donors), and removes from the gap a number of deep levels associated with some transition metal impurities, such as Au. Hydrogen also enhances substantially the diffusivity of interstitial O, and interacts with the crystal. A number of reviews of these properties have recently been published [1–3].

Almost all of what is known experimentally about *isolated* H in semiconductors has been obtained from muon spin rotation (μSR) [4] studies. This technique uses positive muons, which behave like a light isotope of the proton. Except for the smaller mass of the muon ($m_\mu \simeq m_p/9$), the analogy between muonium (μ^+e^-) and hydrogen is excellent. At least three centers analogous to isolated hydrogen have been observed in group IV and group III-V semiconductors. Two paramagnetic signals are identified as neutral muonium at or near the tetrahedral interstitial (T) site [5] ("normal muonium" or Mu) and neutral muonium at a relaxed bond-centered (bc) site [6] ("anomalous muonium" or Mu*) where it forms a three-center two-electron bond. The unpaired electron of Mu* is mostly confined to a nonbonding orbital primarily located on its two Si nearest neighbors (NNs) and therefore does not participate in the bonding. The third μSR signal, labeled μ^+, is either a bare muon or the negative Mu$^-$ ion (their μSR signatures would be identical). However, it has always been interpreted as the positive μ^+. This species is the ionized version of Mu*, i.e., a bc interstitial with no unpaired electron [7]. We label the corresponding hydrogen centers H^T, H*, and H$^+$, respectively. In Si and Ge, it is believed that H$^+$ is somewhat more stable than H*, especially in p-type material. This is due to the fact that removing the odd electron from Mu* stabilizes the bonding. However, since μ^+ is not observed in c-C (up to 1000 K) and since Mu* survives in Si and Ge up to rather high dopant concentrations [4], there is no strong argument in favor of H$^+$ being substantially more stable than H*. The present calculations deal only with the two neutral species.

Except for one electron paramagnetic resonance observation [8] and one preliminary infrared absorption report [9] of H* in Si, attempts at direct experimental studies of isolated H in semiconductors have failed. A likely explanation is that isolated H exists at too low concentrations to be detectable. This is due to the presence of virtually unsaturatable traps—even in material free from dislocations or boundaries—such as shallow dopants (several H's may be trapped at a dopant [10]) or platelets [11]. As a result, the presence of H is often recognized by the changes it induces in the electrical and optical properties of the material.

A priori, one would not expect qualitative differences in the behavior of H in Si and Ge. Both semiconductors have very similar properties, especially around or below room temperature. They crystallize in the diamond structure with bond lengths 2.352 Å (Si) and 2.450 Å (Ge), have indirect band gaps (1.17 eV for Si and 0.74 eV for Ge), and are doped using the same acceptor and donor atoms. Further, the chemistry of {Si,H} and {Ge,H} compounds is qualitatively identical and quantitatively very similar, with Ge-H bond strengths a bit weaker than Si-H ones. For example, the bond strength of H-SiH$_3$ is 3.92 eV while that of H-GeH$_3$ is 3.60 eV. However, whenever identical experiments involving H are done on comparable Si and Ge samples, the results are

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very different, showing that *qualitative* differences do exist.

(1) Thermal effusion (TE) experiments were recently performed [12] on doped Si and Ge. The samples were first exposed to a deuterium plasma for 20 h at the plasma temperature $T_{\rm pl}$. Following this exposure, the total amount of incorporated D and its bonding states were characterized by the TE technique. Typical data have peaks showing D being thermally released from several trapping sites. However, in similarly doped Si and Ge samples, the total amount of D extracted from Si *increases* with $T_{\rm pl}$ while it *decreases* in the case of Ge.

(2) We are aware of only one report [13] of successful hydrogen passivation of a B-doped n-type Ge sample. Other attempts have shown no passivation. For example, in the TE experiments discussed above, no dopant passivation is observed in Ge under conditions that lead to almost complete passivation in Si. Further, no passivation of shallow donors has ever been achieved [1] in Ge even though H passivates P, As, and Sb in silicon.

(3) In high-purity samples and at low temperatures most muons injected into a sample form Mu, the species associated with the T site. Mu dominates at low temperature because the T site is easily accessed, while an expansion of some 35% of a host covalent bond is necessary for the bc site to become a minimum of the energy i.e., for a muon to form Mu* (or μ^+). In Si, the fraction of incoming muons forming Mu is 61%, while 37% form Mu*, and the rest is μ^+. In Ge, 72% of the muons form Mu, but only 8% Mu* and about 10% μ^+. It is known [4, 7] that the bc site is more stable for H in Si (as well as in diamond), and about a third of incoming muons manage to force their way into their most stable state at low temperatures. In Ge, however, only 8% reach the bc site, even though the Ge-Ge bond is longer and weaker than the Si-Si bond, making the needed expansion *easier* to accomplish.

(4) In diamond, the thermally induced Mu→Mu* transition shows that Mu* is the stable species. In Si, a Mu→Mu* transition has also been reported [4] (in irradiated samples). No such transition is observed in Ge. Further, recent rf μSR data [14] show substantial differences in μ^+ fractions between Si and Ge. These experiments monitor the μSR intensities of specific muon species as a function of temperature. In high-resistivity Si, the μ^+ intensity is very small ($\simeq$ 8%) up to some 130 K, then increases abruptly to $\simeq$ 35% (ionization of Mu*), then keeps on increasing irregularly (possibly due to Mu→Mu* → μ^+ conversions) up to about 400 K. At that temperature, nearly 90% of the muons form μ^+. Above 400 K, the intensity rapidly drops to zero because rapid charge-exchange processes render the signal unobservable [15]. Similar measurements in high-purity Ge show that μ^+ is *much less abundant* above 200 K.

(5) Finally photothermal ionization spectroscopy experiments [16] conducted in high-purity Ge samples grown under a hydrogen ambient show that the normally electrically inactive substitutional C and Si form pairs with H and become the shallow acceptors A(H,C) and A(H,Si). Other shallow levels appear because of hydrogenation, such as the D(H,O) donor. Only the activation of substitutional C has been reported [17] in n-type Si.

We have studied the properties of interstitial H in c-C, Si, Ge, and α-Sn, and calculated the relative stability of the various sites. We have also compared [18] the equilibrium properties of the {H,B}, {H,C}, and {H,Si} pairs in Si and Ge in order to find out if any differences in the microscopic properties of these complexes were apparent when comparing Si to Ge. The calculations were done at the *ab initio* Hartree-Fock (HF) level with split-valence basis sets on all atoms and polarization functions on selected atoms. We repeated the isolated H calculations in c-C and Si with the method of partial retention of diatomic differential overlap (PRDDO) [19]. These techniques and their application to defects in semiconductors have recently been reviewed [20].

The host crystals were represented by a molecular cluster containing 14 host atoms and constructed in such a way that both the T and bc sites have two complete host atom shells around them. The surface dangling bonds of the cluster were tied using H saturators, as described in Ref. [21]. Extensive studies of cluster size effects [22] for both isolated H and H-containing complexes have shown that even this small cluster describes the defects quite accurately. The cluster size that can be used at this level of theory for hosts such as Ge or α-Sn is restricted by computational limitations. In the case of H* (bc site), only the first NNs were optimized. We know from similar studies [7] in much larger clusters that second NN relaxations stabilize this site by 0.3 to 0.5 eV. In the case of H^T, no lattice relaxations were included.

Detailed analysis of the {H,B}, {H,C}, and {H,Si} pairs shows that these complexes have very similar properties in intrinsic Si and Ge: the same lowest-energy configurations and electronic structures, comparable stabilities, and the same metastable conformations (for details, see Ref. [18]). As concerning the passivation of shallow acceptors and the formation of the {H,B} pair, the experimental difference discussed above is not due to differences in the microscopic structures. As will be discussed below, it is due to a difference in the capture radius of hydrogen by boron. On the other hand, we predicted [18] that the *neutral* {H,C} pair should be a shallow acceptor in high-resistivity Si as well. However, the activation of C in Si could be masked by the passivation of dopants. Further, the neutral {H,C} pair is a trap for a second H, forming an electrically inactive (but optically active) {H,H,C} complex.

The major difference between Si and Ge appears when studying the relative stability of the various interstitial sites for H as one goes down the periodic table. While in c-C and Si, the bc site is substantially lower in energy than the T site, the T and bc sites become almost energetically degenerate in Ge, and the T site is definitely the lowest in α-Sn. Figure 1 shows the relative energies of the two sites in the four hosts. The zero of the energy corresponds to our cluster with atomic hydrogen far away from it. Note that it always *costs* energy to put H into the crystal. As shown in the figure, H^T becomes more stable than H^* between Si and Ge. This has the following consequences.

(1) The T site is a minimum of the energy regardless of whether lattice relaxations are included in the calculation or not, while the bc site becomes a minimum only if a substantial relaxation of a bond (of the order of 35%) is realized. Thus, even if the bc site is lower in energy, most of the injected muons first stabilize at T sites and must overcome a substantial barrier to reach their lowest-energy configuration. In hosts where the bc site is actually higher in energy than the T site, there is little or no incentive to populate bc sites at all. This prediction is consistent with the low occurrence of Mu^* and μ^+ and the high occurrence of Mu in Ge as compared to Si.

(2) The positively charged species, H^+ (or μ^+), which is the ionized version of bc hydrogen, changes from being very abundant in Si to being almost nonexistent in Ge. In Si, the passivation reaction $B^- + H^+ \longrightarrow \{H,B\}^0$ is characterized by a very large Coulomb capture radius of H^+ by B^-, and is therefore very efficient. In Ge, however, H^+ is rare, and H^0 must stumble almost accidentally upon B^- in order to passivate it; then must capture a hole to finish the process.

(3) Plasma exposure of Si and Ge samples results in the following behavior. In Si at or above room temperature, most of the H self-traps at a bc site where it is bound and mostly in the +1 charge state, thus repelling neighboring H's. Penetration occurs as bc hydrogen hops to a T site (where it is neutral) and diffuses deeper into the bulk, in search of a new trap, such as another bc site (where it easily ionizes again). In Ge, however, almost all of the H finds itself at T sites, in the neutral charge state. The reaction $H^0 + H^0 \longrightarrow H_2$ is highly probable and leads to the formation of an immobile H_2 molecule within the first few layers of the crystal, thus preventing the penetration of atomic H into the bulk. At higher plasma temperatures, individual H^0 atoms are more mobile, and the probability of H_2 formation increases, leading to less penetration.

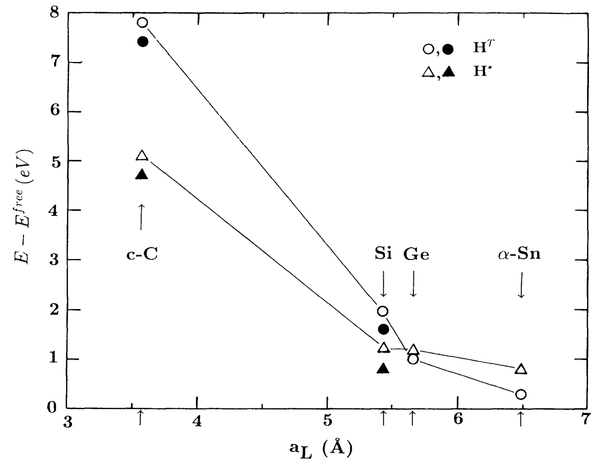

FIG. 1. Energy required insert free atomic H and form H^T (circles) and H^* (triangles) in group IV semiconductor hosts. The zero of the energy corresponds to the perfect cluster and free atomic hydrogen far away from it. Note that the bc site is more stable than the T site only in *c*-C and Si. The open circles and triangles are results obtained at the *ab initio* HF level with split-valence polarized basis sets. The full dots and triangles are results obtained in the same cluster at the PRDDO level. The lines connecting the *ab initio* results are a guide to the eye.

One can understand qualitatively why the energies of H at the T and bc sites vary as shown in Fig. 1 on the basis of simple arguments. The stability of the T site increases with the lattice constant since the calculated energies of H^T converge toward H^{free} for an infinite lattice constant. The stability of the bc site, however, is determined by several factors. First, the optimal bond length (the one that would be realized in free radicals) for bridged bonds involving H is quite long and difficult to realize in hosts with a small lattice constant. For example, the C-H-C bond in diamond has C-H$\simeq$1.1 Å, which is equal to the C-H bond length in two-electron bonds. In Si, a much larger relaxation can be accomplished, leading to Si-H$\simeq$1.6 Å in Si-H-Si, much longer than the 1.4 Å of the single Si-H bond. Thus, increasing the lattice constant helps stabilize this site. Our calculations show that beyond Si, further increases in lattice constant only marginally improve the situation, the bridged bond being already nearly optimal. Second, the bc site becomes less stable as one goes down the periodic table because the bond strengths between H and C, Si, Ge, and α-Sn become weaker. Experimental bond strengths [23] for two-electron bonds are as follows: 4.54 eV for H-CH_3, 3.92 eV for H-SiH_3, 3.60 eV for H-GeH_3, and 3.20 eV for H-$Sn(n\text{-}C_4H_9)_3$. Finally, shorter bond lengths result in greater bonding-antibonding level separations, which would tend to stabilize the bc site for shorter lattice constants.

In conclusion, the change in the relative stability of H^T and H^* results in the virtual disappearance of H^+ in Ge, while H^+ remains quite abundant in Si. In Ge, the absence of H^+ reduces dramatically the capture cross section for acceptor passivation and explains why acceptor passivation is so difficult to achieve. This also affects qualitatively the μSR spectra, where Mu dominates over Mu^* and μ^+. If any μSR thermal transitions are to be expected, they should involve $\mathrm{Mu}^* \rightarrow \mathrm{Mu}$, not the opposite. Finally, since neutral H at the T site is more stable than both bound species (H^* and H^+ at the bc site), the penetration of H into the bulk of plasma-exposed Ge samples is greatly affected since the abundance of mobile H^0 at T sites facilitates the formation of H_2 molecules near the surface. Note that the difference in the penetration of H into the bulk is the only reason we see at this point why donor passivation is more difficult to achieve in Ge than in Si.

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