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Hydrogen in Silicon and Germanium

Michael Stavola
Department of Physics, Lehigh University, Bethlehem, Pennsylvania 18015, USA
e-mail: michael.stavola@Lehigh.edu

Abstract

Hydrogen strongly affects the electrical properties of semiconductors and participates in a surprisingly rich variety of phenomena. This paper surveys the similarities and differences in the properties of hydrogen-containing defects in Si and Ge.

1. Introduction

An understanding of hydrogen and its fundamental properties is vital in semiconductor technology. H introduces electrical levels in the band gap of semiconductors, has different configurations in its different charge states, forms complexes with many impurities and defects, and can also give rise to other H-containing defects such as H_2 molecules. H is ubiquitous in the semiconductor growth and processing environment and is introduced easily into semiconductors intentionally or unintentionally. Once present, H modifies the electrical properties of semiconductor materials and the behavior of electronic devices. The technological implications of such effects are now widely recognized. Ge and SiGe alloys find exciting applications in optoelectronics and microelectronics. The present paper compares and contrasts the properties of H in Si and Ge. In Si, the passivation of defects and impurities has been an important focus, whereas in Ge, the activation of impurities by hydrogen has been emphasized.

It is impossible in this brief survey to discuss, or even to cite, all of the important results. Fortunately, there are several books and review articles that contain further information and references to the literature.[1-9]

2. Diffusivity and solubility

A frequently cited determination of the diffusivity (D) and solubility (S) of hydrogen in silicon was published in 1956.[10] The time dependence of the permeation of H through thin-walled cylinders of Si was studied for the temperature range 1090°C to 1200°C and analyzed to yield the following results:

$$D = 9.4 \times 10^{-3}\ \text{cm}^2/\text{s}\ \exp(-0.48\ \text{eV}/kT); \quad S = 4.8 \times 10^{24}\ \text{cm}^{-3}\ \exp(-1.88\ \text{eV}/kT) \qquad (1)$$

A review of the diffusivity and solubility of H in Si that discusses modern determinations and theory is given in ref. (11). Similar experiments were performed for Ge over the temperature range 800°C to 910°C to yield:[12]

$$D = 2.7 \times 10^{-3}\ \text{cm}^2/\text{s}\ \exp(-0.38\ \text{eV}/kT); \quad S = 3.2 \times 10^{24}\ \text{cm}^{-3}\ \exp(-2.3\text{eV}/kT) \qquad (2)$$

These results are shown in Fig. 1. The diffusivity of H is large for both Si and Ge while the solubility is relatively small. These results are in reasonable agreement with subsequent measurements made at elevated temperatures. For example, Ge crystals were grown in a hydrogen ambient spiked with tritium whose decay was then detected in the grown material.[13] Hydrogen concentrations approximately consistent with Eq.(2) were found.

The results in Eqs.(1) and (2) are sometimes extrapolated to temperatures as low as room temperature. Measurements for the diffusivity of *isolated* H (in its positive charge state) in Si made near room temperature and even near 135K are in remarkable agreement with Eq.(1).[14,15] *However*, the effective diffusivity and solubility of H that are observed in many experiments performed at reduced temperatures are affected dramatically by the interaction of H with other defects or with other H atoms. Equations (1) and (2) would predict a diffusivity near 10^{-7} cm^2/s at 200°C for both Si and Ge and therefore a penetration depth of H near 200 μm (for a 1hr hydrogenation treatment). The solubilities given by Eqs. (1) and (2) for H in Si or Ge at 200°C are negligible. In practice, however, if Si or Ge is treated for roughly 1 hr in a hydrogen plasma at 200°C, an H concentration of $\sim 10^{18}$ cm^{-3} is found in a surface layer ~1 μm thick.[16] For doped Si treated in a hydrogen plasma, the H concentration near the surface mimics the doping concentration and can easily be 10^{17}cm^{-3} or more. In most practical circumstances where H is introduced at high concentrations, the effective diffusivity of H is limited by trapping, an idea that was introduced to explain hydrogen indiffusion profiles observed for Ge.[17] The effective solubility is determined by the formation of hydrogen aggregates (H_2 molecules or platelets) or by the interaction of H with other defects. H turns out to be a more important impurity in Si and Ge than Eqs. (1) and (2) suggest.

3. Isolated hydrogen

Isolated H in semiconductors is the most fundamental H-related defect and has been the subject of many investigations. Theory for the Si host[18,19] has examined hydrogen's three charge states, H^+, H^0, or H^-. The formation energies of these charge states depend on the Fermi level position. In p-type Si, the H^+ charge state is favored, and, in this case, H acts as a donor. The minimum energy configuration for H^+ has the proton located at a

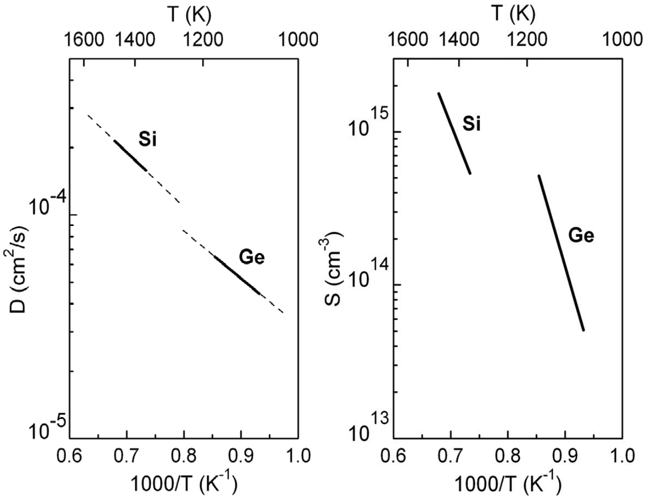

Fig. 1. Diffusivity and solubility of H in Si and Ge. Refs. (10) and (12).

bond center where the electron density of the host crystal is high [Fig. 2(a)]. To accommodate the H atom, there is a large outward relaxation of the Si nearest neighbors. In n-type Si, the H^- charge state is favored, and H acts as an acceptor. The minimum energy configuration for H^- has the H atom near a tetrahedral interstitial site where the electron density of the host is low [Fig. 2(b)]. Theory finds that H^0 is not the stable charge state for any position of the Fermi level and that H is a negative U defect with its donor level above its acceptor level, i.e., with inverted order in the gap.[18-20] As a negative U defect, H has an occupancy level that lies midway between its donor and acceptor levels and whose position with respect to the Fermi level determines the H charge state. Theory also finds that the H(+/-) occupancy level has a universal alignment in different semiconductor hosts with respect to the vacuum level so that the position of the H(+/-) level for any semiconductor can be determined if the band offsets are known.[21]

Isolated H is mobile below room temperature in most semiconductors, making experimental studies of its properties challenging. One method to produce isolated H is by the implantation of protons into samples held at cryogenic temperature so that H diffusion is frozen out. Isolated H in Si has been studied by electron paramagnetic resonance (EPR),[22-24] IR spectroscopy,[25] and deep level transient spectroscopy (DLTS).[26] These data provide information about the structure, electronic properties, and migration of H. H in Si is found to have a donor level at E_c-0.16 eV when in the H^+ charge state. H has a deep acceptor level near mid-gap when in the H^- charge state.

For protons implanted into Ge at cryogenic temperatures, infrared absorption experiments have revealed the vibrational properties of H^+ and H^-.[27] The spectrum for H^+ is consistent with the H atom at a bond center site, whereas the spectrum for H^- is consistent with the H atom close to the tetrahedral site. DLTS experiments have also been performed for Ge implanted with protons.[28] In this case, a donor level is found at E_c-0.11 eV. No acceptor level was found, consistent with its being resonant with the valence band.

A rich source of information about H in semiconductors is provided by experiments on muonium (Mu), a light pseudo-isotope of H.[5,29-31] μ^+ is a particle with spin ½ and a mass about one-ninth that of a proton. When an energetic beam of muons is stopped in semiconductors, muonium centers are formed whose properties mimic those of H. The lifetime of the muon is only 2.2 μs, therefore, in most cases, it decays before it has time to interact with other defects and impurities. Elegant methods have been developed to study the muon spin polarization and to determine hyperfine structure for muonium centers. A configuration with the muon at a bond-center site, $Mu_{BC,}$ and a configuration with the muon at a tetrahedral interstitial site, $Mu_{T,}$ have been identified, and each configuration can have different charge states, Mu_{BC}^0, Mu_{BC}^+, Mu_T^0, and Mu_T^-. Recent studies have focused on the transitions between the different configurations and charge states.[30,31] Where comparable results exist, muonium and H have been found to have similar properties. The properties of muonium have been studied for a variety of semiconductors and are consistent with the existence of a universal Mu(+/-) occupancy level.[32,33]

The positions of the donor and acceptor levels of isolated H in the band gap and, therefore, the H(+/-) occupancy level, determine which charge state will dominate for different positions of the Fermi level, and similarly for muonium. The acceptor and donor levels for muonium in Si and Ge and the Mu(+/-) occupancy level are shown in Fig. 3.[32,33] The positions of the levels for isolated H determined by experiment give a very similar picture. For Si, the experimental H(+/-) occupancy level lies in the upper half of the band gap. Therefore, the H^+ charge state will dominate in Si that is intrinsic (low doping or elevated temperature) with its Fermi level at mid gap.[20] For Ge, the experimental H(+/-) occupancy level lies below midgap.[33] Therefore, the H^- charge state will be more important in intrinsic Ge than in Si. (In proton implanted Si and Ge, implantation damage should pin the Fermi level at mid gap. Only H^+ has been seen by IR spectroscopy for Si, whereas for Ge, both H^+ and H^- were seen.)

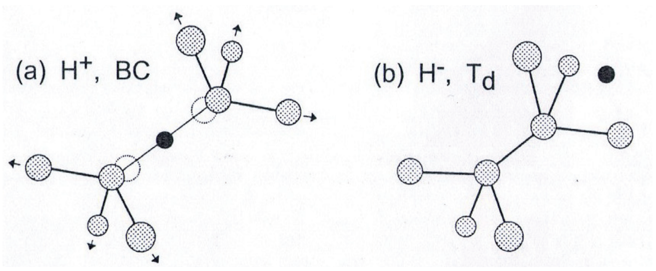

Fig. 2. Location of (a) H^+ and (b) H^- in Si. Ref. (20).

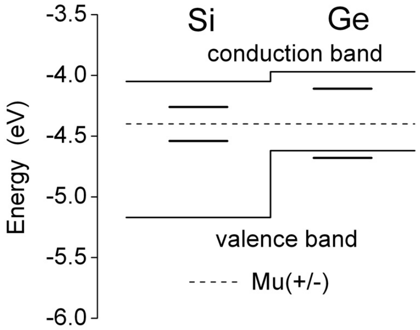

Fig. 3. Levels for Mu in Si and Ge. Upper level is the donor level, and the lower level is the acceptor level. Ref. (33).

4. Impurity-hydrogen complexes

It is possible for H to passivate or activate impurities in semiconductors, and in this regard, Si and Ge appear to be quite different. In Si, the passivation of shallow impurities has been studied extensively, whereas in Ge, isoelectronic impurities have been found to be activated by H. While there are examples of the activation of impurities in Si, none has attracted the tremendous attention devoted to the passivation of shallow dopants.

Passivation of shallow impurities. For Si, as for many other semiconductors, the shallow impurities used to control conductivity can be passivated by hydrogen.[1-9] For boron-doped Si, it was. found that a high resistivity surface layer was created by the indiffusion of H.[34,35] To explain the passivation of shallow acceptors in Si, it was proposed that atomic H introduces a *donor level* in the semiconductor band gap.[36] The electron from the H donor recombines with the hole associated with the acceptor impurity, thereby making *compensation* of the acceptor the first step toward passivation. H^+ is mobile and is attracted to the charged acceptor A^-. The two charged species become covalently bound to form a neutral acceptor-H complex, completing the *passivation* of the acceptor. These steps are given in the following expression:

$$(H^+ + e^-) + (A^- + h^+) \rightarrow H^+ + A^- \rightarrow (H\ A)^0.$$

Because H is amphoteric in Si, shallow donor impurities such as P can also be passivated by H.[37] In n-type material, atomic H introduces an *acceptor level* in the semiconductor band gap, leading to the compensation of the shallow donor.[38,39] The mobile H^- is attracted to the positively ionized donor and these charged species become covalently bound to form a neutral complex.

The structures of the acceptor-H and donor-H complexes in Si have been studied by a variety of experimental methods and theory. For the acceptor-H complexes, the H atom sits near the bond center between the acceptor impurity and a neighboring host atom [Fig 4(a)]. For the donor-H complexes, the H atom is located at an antibonding site and is bonded to one of the donor impurity's Si neighbors [Fig. 4(b)].

Unlike for Si, the passivation of shallow impurities in Ge has not been studied exhaustively. It has been suggested that complexes of H with acceptors and donors in Ge are not very stable thermally.[40,41] However, hints of passivation have been found; the passivation of shallow impurities has been suggested as a possible cause of the spatial variation of the conductivity found for as-grown crystals of ultra-pure Ge.[13,17] Furthermore, the thermal stability of the hydrogen passivation of B in Ge was studied by Hall measurements, and the electrical activity of the passivated B acceptor was recovered by a brief anneal at 100°C, confirming the low thermal stability of the acceptor-H complex.[1]

Activation of impurities. Unintentional shallow centers were discovered in ultrapure Ge that had been grown in a hydrogen ambient and that was rapidly quenched from 400° to room temperature.[42,43] Immediately following quenching, shallow acceptor centers are formed. A donor center is then formed if the sample is held at room temperature and remains stable up to near 100°C. Because the concentration of these defects is small ($< 10^{11}$ cm^{-3}), they were studied by the highly sensitive, photo-thermal-ionization spectroscopy in a Fourier spectrometer to reveal their detailed electronic structure.[43-46] An isotope shift of the electronic lines upon the substitution of D for H proved the involvement of hydrogen.[44]

The shallow acceptor centers in the Ge host are labeled A(H,Si) and A(H,C) and were assigned to complexes in which H^- is weakly bound to substitutional Si or C which are isoelectronic impurities that are introduced into ultrapure Ge during growth (from the quartz or graphite crucibles that contain the melt).[45,46] The A(H,Si) and A(H,C) centers have trigonal symmetry,[46] and theory has found that the H atom lies near the T site of the lattice.[47] The donor center in Ge was labeled D(H,O) and assigned to a complex with H bound to interstitial oxygen.[48]

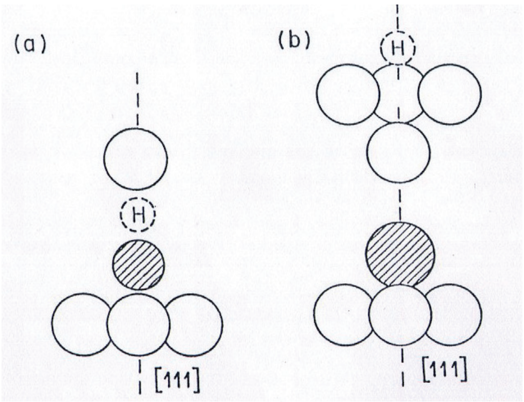

Fig. 4. Acceptor-H and donor-H complexes in Si.

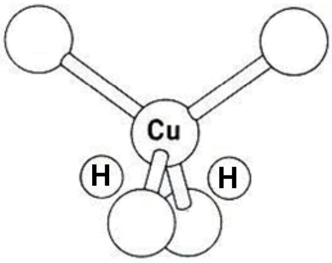

Fig. 5. CuH_2 complex in Ge. Ref. (59).

In the Ge host, the Si and C impurities are not electrically active until they are activated by weakly binding a hydrogen atom. In ultrapure (intrinsic) Ge, where the Fermi level will lie above the H(-/+) occupancy level, the negative charge state of isolated H will occur. H^- becomes weakly bound to the substitutional Si or C impurities to form the shallow acceptors that are observed.

While Ge comes to mind when the activation of impurities is considered, there are examples in the Si host. Substitutional C in Si weakly binds H to form a donor defect with a level at E_c-0.16 eV.[49] This defect is reminiscent of the A(H,C) center in Ge except that for the Si host, it is H^+ that is bound to C to form a donor rather than an acceptor. Another example of activation in Si is the E_3'' center in which interstitial oxygen binds an H atom.[26]

Hydrogenated transition metals. One of the early motivations for the study of H in semiconductors was its ability to passivate deep-level defects. For Si and Ge, it was shown that the exposure of a sample to a hydrogen plasma can eliminate electrical levels associated with transition-metal impurities.[50,51] However, in these early studies, little was known about the microscopic properties of the hydrogenated defects or about how H affects the electronic states. For Si, new results have come from a variety of approaches. Wet-chemical etching has been used to introduce H into thin surface layers of Si samples that also contained a transition-metal impurity.[52,53] In these studies, many transition-metal-H complexes were discovered and studied by DLTS. It was found that there are families of complexes that include different numbers of H atoms, for example, PtH, PtH_2, PtH_3, and PtH_4.[54] Of these, only PtH_4 is believed to be passivated; the other centers remain electrically active. In other studies, it was found that H could be introduced throughout bulk Si samples by annealing in H_2 gas at elevated temperature (1250°C) and that Pt and Au impurities could be hydrogenated by this method.[55-57] Hydrogenated defects like PtH and PtH_2 were discovered and studied by structure-sensitive EPR and IR spectroscopies. In these studies, it was also found that the defects are electrically active.[55-58]

For Ge, a hydrogenated transition-metal impurity with particularly interesting properties is Cu.[59] Substitutional Cu is a triple acceptor in Ge that can be passivated in steps by the addition of H atoms. For example, the addition of two H atoms gives rise to a CuH_2 complex that is a single acceptor. The CuH_3 center is suggested to be fully passivated.[60] For the CuH_2 center, the electronic ground state is split into a manifold of levels.[59] When H is replaced by deuterium or tritium, a single ground state level is seen, leading to the conclusion that the complicated ground state for the CuH_2 center is due to the tunneling of the H atoms about the Cu atom. There are other centers in both Si and Ge for which the tunneling of the light H atom is important.[48,61]

The proposed structure[59] for the CuH_2 complex in Ge is shown in Fig. 5. Recent theory finds a similar structure for a CuH_2 complex in Si.[62] While these results suggest that the transition-metal-hydrogen complexes in Si and Ge have similar structures, the precise location of the H atoms remains controversial.

5. Hydrogen interactions with native defects

The native vacancy and interstitial defects whose dangling bonds are terminated by H atoms are an important class of H-containing defects. In a pioneering study, Si was implanted with protons at room temperature, producing many new H vibrational-absorption lines.[63] In these experiments, the energetic protons create vacancy and interstitial defects whose dangling bonds then become bonded to the implanted H. After many years of study, a number of defects have been identified definitively.[64-67] There is a family of vacancy-H complexes (VH_n) for which H terminates different numbers of dangling bonds of the vacancy.[64] There is an IH_2 defect for which the dangling bonds of a Si interstitial are terminated by H atoms.[65] And there is a hydrogen dimer called H_2^* that includes one H atom at a bond-centered site and a second at an antibonding site along the same <111> direction.[66] The structures of a few of these defects are shown in Fig. 6.

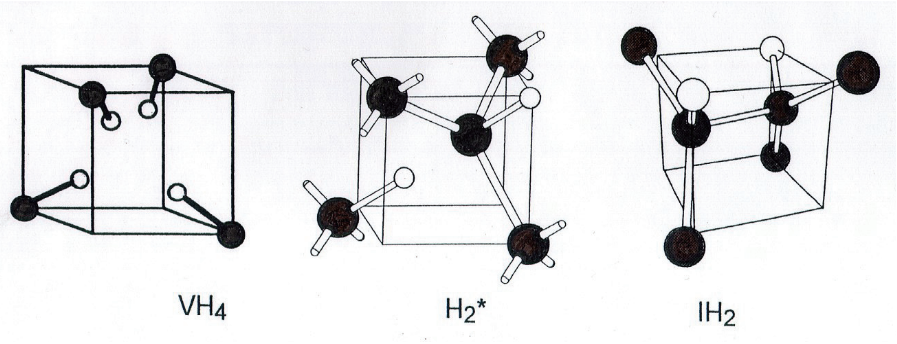

Fig. 6. Structures of the VH_4, H_2*, and IH_2 defects. [B. Bech Nielsen *et al.*, Phys. Rev. B **39**, 3330 (1989) and refs. (66), and (65)].

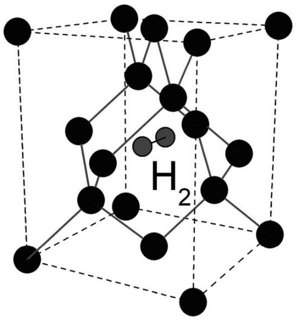

Fig. 7. Interstitial H_2 molecule.

The same defects involving native defects and hydrogen that are formed by the implantation of protons into Si also form in Ge. These defects, VH_n, IH_2, and H_2*, have structures and vibrational properties that are remarkably similar for the two hosts.[25,65,68,69]

An acceptor level at E_v+80 meV that affects the conductivity of dislocation-free, ultrapure Ge has been associated with a V_2H defect.[43,70] Because of its low concentration, structure-sensitive data are not available, and a structure for this defect has not been proposed.

6. Hydrogen molecules

In addition to interacting with defects in semiconductors, H can also form H_2 molecules (Fig. 7). In the early 1980s, theory showed that an H_2 molecule in Si would sit at a T_d interstitial site.[71.72] H_2 also has been suggested to play an important role during the indiffusion of H.[17] The stretching vibration of an interstitial H_2 molecule in a semiconductor was observed first in GaAs by Raman spectroscopy in 1996 and has a frequency of 3934 cm^{-1}.[73] The H_2 line is split by 8 cm^{-1}, leading to the conclusion that this doublet is due to the ortho- and para-H_2 species and, therefore, that the H_2 molecule is freely rotating. Subsequently, a vibrational line for H_2 in Si at 3618 cm^{-1} was discovered by Raman and IR spectroscopies.[74,75]

For a few years, the experimental data for H_2 in Si presented a vexing puzzle and appeared to suggest a low-symmetry static defect. Theory, however, found no evidence for a substantial barrier to the nearly free rotation of interstitial H_2.[76-80] IR absorption experiments for the HD molecule in Si and their interpretation led to the recognition that the experimental properties of H_2 in Si can be explained in terms of a nearly free rotator, similar to the situation in GaAs.[81,82] A subsequent Raman study found vibrational lines for both the ortho and para H_2 species in Si at 3618 and 3627 cm^{-1}.[83]

A recent study has extended results for H_2 in semiconductors also to Ge. Vibrational lines for the ortho and para H_2 species in Ge were found at 3826 and 3834 cm^{-1} by Raman spectroscopy.[84] These vibrational frequencies were also found to be consistent with the results of theory.

A trend in the vibrational frequencies for H_2 in several semiconductor hosts was predicted by theory.[77] The vibrational frequency for H_2 in a semiconductor was found to be lower than for H_2 in gas phase (4161 cm^{-1}) because the electron density at the T site of the crystal lattice weakens the H-H bond and reduces the vibrational force constant. As the semiconductor lattice constant decreases, the electron density at the T site increases. Therefore, the H_2 vibrational frequency will be reduced as the lattice constant for the semiconductor host is reduced. The experimental vibrational frequency for H_2 in Ge is a few hundred cm^{-1} greater than that of H_2 in Si, similar to H_2 in GaAs. Because the lattice constant of Ge (5.646Å) is larger than that of Si (5.431Å) and is similar to the lattice constant of GaAs (5.653Å), the trend in the vibrational frequencies for H_2 in GaAs, Ge, and Si is qualitatively consistent with the prediction of theory.[77]

7. Conclusion

At first glance, the effect of H in Si and Ge seems to be quite different. In Si, the passivation of dopants and defects has been the focus of many studies. In Ge, the activation of impurities in ultrapure Ge and the physics of tunneling centers have been emphasized. However, a closer look reveals that the physics of hydrogen in Si and Ge is more similar than the emphasis placed on results in the literature might suggest.

Similar to Si where dopant passivation has been studied extensively, acceptor passivation has been reported also for Ge. However, because of the low thermal stability of dopant-H complexes in Ge, these defects have not been studied in detail. The activation of impurities by hydrogen in Ge has been the focus of much attention because of the effect such defects have on the conductivity of ultrapure Ge. Activated impurities have also been reported for Si, but in this case, the activation of impurities has not played an important role in Si technology because of their low thermal stability. The hydrogenation of deep levels appears to be similar in the two hosts, with the proposed structures of transition-metal-hydrogen complexes and native-defect-H complexes being the same. The formation and physics of hydrogen molecules in Si and Ge are also similar.

An interesting difference between Si and Ge is the position of the H(+/-) occupancy level of isolated hydrogen.[32,33] In intrinsic Si, H^+ should dominate whereas in intrinsic Ge, recent results suggest that H^- might be important. However, in terms of the diffusion and solubility of isolated H at elevated temperature and the physics of the hydrogenated defects that occur, this difference seems to be important only for the appearance of H^- in proton implanted Ge and for the defect complexes in which H^- is weakly bound to isoelectronic impurities.

Have the very different technological applications of Si and ultrapure Ge rather than the physics of the defects and defect processes that are involved led to the different focuses on hydrogen passivation and activation in these materials? As Ge becomes the focus of new applications in microelectronics and optoelectronics, it will be fun to see what interesting and unusual properties of H emerge, as they often have for other host materials.

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