# Hydrogen Defect-Level Pinning in Semiconductors: The Muonium Equivalent

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We have determined locations for the donor and acceptor levels of muonium in six semiconductor materials (Si, Ge, GaAs, GaP, ZnSe, and 6H-SiC) as a test of defect-level pinning for hydrogen. Within theoretical band alignments, our results indicate a common energy for the equilibrium charge-transition level Mu$(+/-)$ to within experimental uncertainties. However, this is nearly 0.5 eV higher than the energy at which the equivalent level for hydrogen was predicted to be pinned. Corrections for zero-point energy account for only about 10% of this difference. We also report experimental results for the (negative-$U$) difference between donor and acceptor levels for Mu to be compared with calculated values for H impurities in the same materials.

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Hydrogen has long been known as a chemically active impurity in semiconductor materials [1], where it reacts with other impurities and more extended defects to alter the electrical and optical properties associated with those defects. Hydrogen is routinely used in semiconductor technology as a passivation agent to remove unwanted electrically active defect levels from the band gap, thereby eliminating deleterious effects on device performance and lifetime. In some cases, H has an electrical activity of its own, functioning as a shallow donor dopant in materials with high electron affinities such as ZnO or InN and perhaps as an acceptor in a few others.

Hydrogen occurs in three charge states ($H^+$, $H^0$, and $H^-$) and is a negative-$U$ impurity in many materials, opposite to expectations when there are more than two charge states for an impurity at a single site. Here $U$ denotes the total energy cost of adding a second electron to an impurity. If there is a site change associated with the neutral to negative charge-state transition, the decrease in lattice energy may offset the electrostatic repulsion and this total energy difference can be negative. In that case, the donor level, the electron chemical potential (Fermi energy, $E_F$) at which positive and neutral charge states should have equal populations in equilibrium, lies above the acceptor level where neutral and negative populations are equal. With increasing $E_F$ the dominant equilibrium charge state then changes directly from positive to negative at the $(+/-)$ level, located halfway between the inverted acceptor $(-/0)$ and donor $(0/+)$ levels.

Based on their theoretical results for a number of materials, Van de Walle and Neugebauer [2] predicted that this charge-transition level for hydrogen, H$(+/-)$, should be universally pinned at a specific energy on an absolute scale independent of the host material. Here we report results of an experimental test of these predictions for the muonium (Mu) isotope of H in a series of semiconductor materials. Our measurements place the Mu donor and acceptor levels with respect to either the conduction or valence band edge, but they must rely on theoretical band locations for an absolute energy for Mu defect levels.

Muonium defect centers are formed when positive muons are implanted into semiconductor materials and have been investigated for many years [3–5] as an analog of isolated hydrogen impurities. Mu is much easier to access experimentally than isolated H. Much of the data used to test computational results for H [6] has historically come from muon spin research ($\mu$SR), a collection of magnetic resonance related techniques (see Ref. [7]) that make use of 100% spin-polarized muon beams.

The as-implanted mix of muonium states is far from equilibrium and includes metastable sites and charge states. The temperature dependence for the $\mu$SR signatures of observed Mu states provides information on transitions that move the Mu defect system toward equilibrium, with each process becoming visible as transition rates fall into the microsecond sensitivity range. The muon lifetime of 2.19 $\mu$s, its Larmor frequency of 135.5 MHz/T, and hyperfine frequencies for $Mu^0$ states control $\mu$SR's sensitivity to various transitions.

The materials included in this investigation were selected because (at least) two distinct $Mu^0$ states are found in each, providing for the possibility of observing both the Mu donor and Mu acceptor ionization transitions that directly place the associated thermodynamic defect levels relative to the band edges. For primarily covalent diamond (Si, Ge) and zinc blende (GaAs, GaP) structured semiconductors the bond-centered (BC) location is the lowest energy site for $Mu^0$ and $Mu^+$; thus, the BC site is the donor location. The tetrahedral interstitial region (T site) for elemental semiconductors is the stable location for $Mu^-$ and supports a highly mobile metastable $Mu^0$ center, and thus represents the acceptor site. The two neutrals have

 

very different hyperfine characteristics [3,4], making identification of $Mu^0$ states straight forward. For slightly ionic III-V compounds, the $T_{III}$ site is the acceptor location and the $T_V$ site becomes a metastable location for a high-temperature mobile $Mu^+$ state [8]. ZnSe and SiC do not fit into this generic description, as discussed later.

Figure 1 is a generic formation energy diagram showing relationships among the Mu centers expected in a cubic semiconductor for which $Mu^0_{BC}$ is observed. The points at which formation energies are equal for the lowest energy sites for two charge states (vertical arrows) represent the thermodynamic defect levels we are seeking. The crossing points marked by circles are the energies we are best able to directly measure: the muon remains at a single site during these accessible charge-state transitions. We must make an adjustment as per Fig. 1 to obtain the proper acceptor level in most cases. For GaAs and Ge we determined this correction experimentally [9,10] and have made an estimate for other materials. Below, we briefly discuss measurements used to extract donor and acceptor levels for Mu in the six materials of this study and compare with data for H where it exists.

*Silicon.*—As indicated above, the $Mu^0_{BC}$ ionization energy places the donor level with respect to the conduction band minimum. The most accurate results are usually obtained from the $Mu^0_{BC}$ relaxation rates versus temperature. Early data for Si [3] gave 0.17 eV but with a large uncertainty. We have instead used temperature-dependent amplitudes for the $Mu^+_{BC}$ final state from rf-$\mu$SR resonance results [11] which yield $0.21(\pm 0.01)$ eV.

Acceptor (hole) ionization of $Mu^0_T$ could not be directly observed in Si because the T-to-BC site change for $Mu^0$ occurs much faster in near-intrinsic and $p$-type samples, while electron capture dominates transitions out of $Mu^0_T$ in $n$-type material [11]. However, the T-site Mu acceptor level in Si has been determined relative to $E_C$ based on thermal loss of an electron from $Mu^-_T$. The data were temperature- and field-dependent depolarization rates [12] resulting from the rapid $0/-$ charge cycles for $Mu_T$ that are triggered by this transition in a $10^{16}$ cm$^{-3}$ $n$-type sample. This result gives excellent balance for Mu levels in the SiGe alloy system [13] and places the $T(-/0)$ level in Si at $E_C - 0.60(\pm 0.04)$ eV. Our estimated adjustment to the acceptor level due to $Mu^0$ site metastability is $+0.12$ eV, placing $Mu(-/0)$ at $E_C - 0.48(\pm 0.07)$ eV, with most of the uncertainty in the correction factor. We thus locate the charge-transition level $Mu(+/-)$ at $E_C - 0.34(\pm 0.04)$ eV for the Mu isotope of H in silicon.

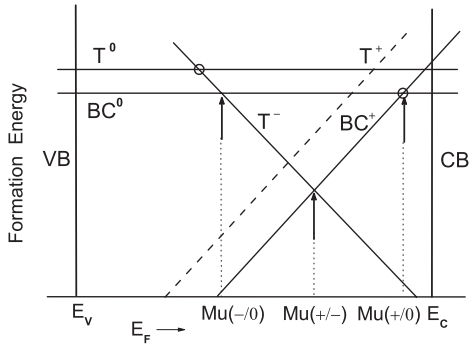


FIG. 1. Formation energies for stable and metastable Mu centers in cubic semiconductors as a function of $E_F$. Vertical arrows mark the Mu defect levels; circles mark experimentally accessible points; the dashed line is for the $T_V$ donor site in III-V compounds.

Deep-level transient spectroscopy (DLTS) measurements [14,15] following low-temperature proton implantation provide the hydrogen donor and acceptor levels in silicon. Annealing curves place $H(0/+)$ at $E_C - 0.175$ eV, shallower than $Mu(0/+)$ by $\sim$35 meV, and give a T-site acceptor level at $E_C - 0.65$ eV based on the same transition as used for Mu. We expect the correction for a metastable $H^0$ to be slightly smaller than for Mu, and estimate that $H(-/0)$ is near $E_C - 0.55$ eV, about 0.07 eV deeper than for Mu. These estimates put $H(+/-)$ only 20 to 30 meV deeper than $Mu(+/-)$ with a larger uncertainty on each placement, and imply that $-U$ will be slightly larger for H.

*Germanium.*—Early $\mu$SR data [3] show that both the BC and T-site neutral signals disappear below $\sim$110 K in Ge. We assigned these transitions to bidirectional site changes [10] for $Mu^0$ because amplitude growth for the ionic charge states gave very different energies. Recent spin precession measurements under optical excitation [16] separate the $Mu^+_{BC}$ and $Mu^-_T$ contributions. The BC fraction is relatively insensitive to the optical excitation and yields a smaller $Mu^0_{BC}$ ionization energy than was claimed earlier [10] from less direct measurements. These data place the $Mu(0/+)$ donor level at $E_C - 0.145(\pm 0.016)$ eV in Ge, much more consistent with the DLTS results [17] that put $H(0/+)$ at $E_C - 0.110$ eV.

Longitudinal depolarization data for ultrapure Ge [10] show an electrically inactive state that disappears with a characteristic energy larger than the Ge band gap. We assigned [18] this state to $Mu^-$ and have confirmed [13] that the Mu acceptor level lies within the valence band for bulk SiGe alloys having less than $\sim$9% Si content. These results imply that the $Mu(-/0)$ acceptor level lies below $E_V$ by about $0.085(\pm 0.010)$ eV at 350 K. Based on these numbers, the $Mu(+/-)$ level is about $0.115(\pm 0.010)$ eV below the midgap for germanium. The H acceptor level has not been observed for Ge, consistent with a band-resonant location.

*Gallium arsenide and gallium phosphide.*—Results for muonium properties in these two III-V compounds are qualitatively very similar and come from equivalent techniques. We recently published [9] a detailed account of results for Mu in GaAs. The BC ionization energy places the Mu donor level at $E_C - 0.173(\pm 0.005)$ eV in GaAs using temperature-dependent relaxation rates for $Mu^0_{BC}$

hyperfine lines from several samples. The DLTS result [19] for the H donor level is $E_C - 0.141(\pm 0.001)$ eV. Relaxation rates for $Mu^0_{BC}$ in one GaP sample put the donor level at $E_C - 0.15(\pm 0.02)$ eV.

For both GaAs and GaP, the data used to place the Mu acceptor levels were a step in rf-$\mu$SR resonance amplitudes assigned to the final state of the $Mu^0_T \rightarrow Mu^-_T + h^+$ ionization transition. These assignments are supported by spin precession results [9] that confirm the $Mu^-$ final state in GaAs. The offset for T-site energies from those of BC sites was determined experimentally [9] for GaAs using the BC-to-$T_V$ transition for $Mu^+$ and barriers to $Mu^+$ motion for both sites. This gave a small 43 meV correction from the T-site ionization energy, yielding a Mu(−/0) level at $E_V + 0.595(\pm 0.062)$ eV in GaAs. Similar rf resonance data for GaP put the T-site acceptor level at $E_V + 0.82(\pm 0.09)$ eV.

When all of these results and the associated uncertainties are put together, we claim [9] a Mu(+/−) level in GaAs at $0.21(\pm 0.03)$ eV above the midgap. Without attempting to make a detailed adjustment for the metastable $Mu^0_T$ state, we estimate that Mu(+/−) is about 0.34 eV above the midgap in GaP.

*Zinc selenide.*—Even though the II-VI compound ZnSe has the zinc blende structure, we treat it as a special case because $Mu^0_{BC}$ is not observed. Two isotropic $Mu^0$ centers are seen [20], both with large hyperfine parameters. One model assigns these to immobile $Mu^0$ centers in the two inequivalent T sites. One neutral converts to the other [20] below 40 K, and the final state is identified as residing at the $T_{Se}$ donor site by satellite lines in the microwave resonance spectrum characteristic of $^{77}$Se neighbors (7.6%) with $I = 1/2$.

This $Mu^0$ resonance decreases in amplitude near 50 K and grows again above 200 K before finally disappearing near 350 K. Although questions remain regarding processes responsible for the lower temperature transitions [21], we assign the 350 K transition to Mu donor ionization. Temperature-dependent resonance amplitudes locate the donor level associated with the $T_{Se}$ site at $E_C - 0.40(\pm 0.07)$ eV.

There are several small-amplitude transitions between 250 and ~500 K in various ZnSe data sets [22] that involve either $Mu^+$ or $Mu^-$ but are not definitively identified. However, growth of the diamagnetic amplitude toward the full muon fraction above 650 K appears as a single transition in a few cases. When viewed in conjunction with the identified donor level and theoretical expectations, this high-temperature transition becomes a strong candidate for Mu acceptor ionization, placing Mu(−/0) at $E_V + 1.44(\pm 0.15)$ eV in ZnSe.

*Silicon carbide.*—We have identified strong candidates for both the Mu donor and acceptor ionization transitions in the 6H hexagonal polytype of SiC [23] based on low-field spin precession measurements. Thus far, these diamagnetic amplitude steps have not been coupled with specific $Mu^0$ initial states. The lowest energy location for both $Mu^0$ and $Mu^-$ in SiC is a $T_{Si}$ site [24]. No BC $Mu^0$ signals are observed, but there are three other isotropic $Mu^0$ states seen in 6H-SiC. We have made tentative site [25] and transition [23] assignments based on transition features in $n$-type, $p$-type, and high-resistivity samples. An energy of $E_V + 0.86(\pm 0.04)$ eV is assigned to the Mu acceptor level associated with the $T_{Si}$ site, and a donor level is observed at $E_C - 0.28(\pm .02)$ eV from transition steps in high-resistivity material [23].

The overall results and our conclusions from this study are summarized in Fig. 2 and Table I. We use the relative band alignments and theoretical energy scale of Ref. [2] but add an "experimental" scale that we initially applied to SiGe alloys [13] based on well-defined electron affinities for Si and Ge [26]. Bulk affinities for the polar materials are not nearly as well established. Table I lists the Mu defect-level positions as described in the text, along with a simple determination of $-U$ for each material, without compensating for large temperature differences between features used to extract Mu donor and acceptor energies.

There are two main conclusions that we want to stress. First, within the theoretical band alignments our results for Mu(+/−) as the midpoint between the Mu(−/0) acceptor and Mu(0/+) donor levels are fully consistent with a common energy for the primary equilibrium charge-transition level in these six materials. This supports the main theoretical claim that initiated this investigation. However, our second important result is that the Mu(+/−) level lies almost half an eV above the energy originally predicted for H(+/−), as demonstrated in Fig. 2. Assuming no large offset between the defect-level pinning for H compared to Mu, several additional materials such as InAs should be doped $n$-type by hydrogen. Furthermore, several materials for which the theoretical H(+/−) level fell in the valence band, such that hydrogen was predicted to be a $p$-type

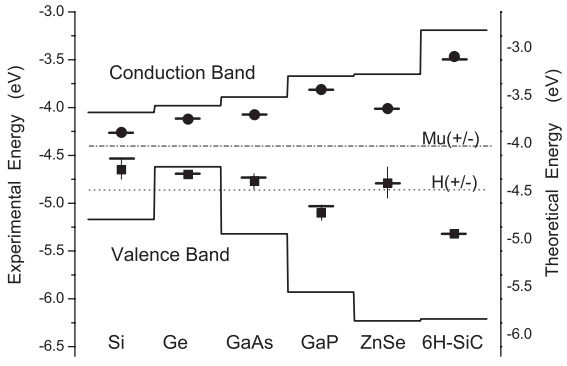


FIG. 2. Results for Mu defect levels: upper bar is the donor and lower bar is the acceptor level for each material; points are measured single-site levels. The dot-dashed and dashed lines represent our result for Mu(+/−) and the theoretical H(+/−) level [2], respectively.

TABLE I. Experimental results on thermodynamic defect levels for the Mu isotope of H in six semiconductors. Energies are in eV.

| Material | $D(0/+)$ from $E_C$ | $A(-/0)$ from $E_V$ | $(+/-)$ level from midgap | $-U$ |
|---|---|---|---|---|
| Si: | −0.21(1) | +0.64(7) | +0.22(4) | 0.27(7) |
| H | −0.175(5) | +0.57(6) | +0.19(3) | 0.38(6) |
| Ge: | −0.145(16) | −0.08(1) | −0.12(1) | 0.60(2) |
| H | −0.110(4) | | | |
| GaAs: | −0.173(4) | +0.60(6) | +0.21(3) | 0.65(6) |
| H | −0.141(1) | | | |
| GaP: | −0.15(2) | +0.82(9) | +0.34(5) | 1.35(10) |
| ZnSe: | −0.40(7) | +1.44(15) | +0.53(10) | 0.75(18) |
| 6H-SiC: | −0.28(2) | +0.86(4) | +0.29(3) | 1.88(5) |

dopant, no longer fall into that category, specifically Ge, GaSb, and InSb.

A few comments are in order with respect to expected differences between hydrogen and muonium energies. The main differences are rooted in the zero-point vibrational states of these two species: in a simple harmonic model Mu would have a factor of 3 larger zero-point energy (ZPE) given the factor of 9 reduction in mass. Thus, the lowest Mu vibrational level approximately corresponds to the first excited state for H in the same potential well. For a donor at the BC site, the bond is weaker for the neutral compared to positive charge state because the additional electron is in an antibonding orbital. The change in ZPE between the two charge states implies that the donor level ought to be deeper in the gap for Mu than for H. This is borne out experimentally for Si, Ge, and GaAs where this difference is 30–35 meV in each case.

For the T-site acceptor there may be larger consequences since most models have four potential energy minima off-center toward the nearest neighbors, with a local maximum at the T site and low barriers for motion among these local minima. A neutral hydrogen may localize in one of these minima, while the larger ZPE for Mu centralizes it at the T site. The negative ion has a large enough radius that very little motional freedom remains for either H or Mu. The extra ZPE for $Mu^0$ then implies that its acceptor level should be higher in the gap than that of H. This is true experimentally for Si, the only comparison available. Based on the experimental numbers for silicon, we expect the shift in $(+/-)$ level between H and Mu more generally to be ∼50 meV or less with Mu slightly higher. These arguments also imply that $-U$ is larger for H than for Mu, a difference in Si of ∼110 meV.

Finally, there are theoretical reasons [27] to expect a small systematic shift in calculated energies that would move $H(+/-)$ toward our placement of $Mu(+/-)$. With our estimate of the offsets between Mu and H defect levels, the $Mu(+/-)$ level we obtain implies that the energy for $H(+/-)$ with respect to vacuum (experimental scale) is close to what was originally predicted. A systematic downward shift in calculated band energies of Ref. [2] by ∼0.4 eV would then be fully consistent with our results.

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