Nature of charged muonium in GaAs with an applied electric field

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(Received 26 January 2005; published 7 July 2005)

We have identified the muonium signal that is enhanced by an electric field in semi-insulating GaAs at 10 K. Experiments were conducted with the electric field applied parallel and antiparallel to the incoming muon. For fields in the range ≈1–15 kV/cm in both directions the nuclear dipolar broadening of the muon spin precession signal at 1 T is consistent with that of positively charged muonium (i.e., Mu^+). This is confirmed by muon-nuclear level crossing measurements at ±20 kV/cm which show a resonance signal identical to that of isolated Mu^+ seen previously in *p*-type GaAs. These measurements show by direct spectroscopic means that the electric field of either direction enhances the probability to form isolated Mu^+ in high resistivity GaAs and are in agreement with a model in which the electric field prevents the formation of neutral bond centered muonium.

DOI: 10.1103/PhysRevB.72.033201 PACS number(s): 71.55.Eq, 76.75.+i, 76.60.Gv

Hydrogen (H) is now well-established to be an important impurity in semiconductors. It is easily introduced into a material and ultimately results in dramatic modifications of the electrical and optical properties of the host. Such changes often occur because H rapidly forms complexes with other impurities intentionally introduced into the semiconductor. This high reactivity means significant difficulty in studying the precursor isolated H centers. Nonetheless, it is still possible to indirectly gather experimental information on isolated hydrogen in many semiconductors by studying muonium ($Mu=\mu^+e^-$). The muonium atom can be regarded as a light short-lived isotope of hydrogen ($m_\mu \approx 1/9 m_p$) with an almost identical electronic structure. The muon lifetime of 2.2 μs strongly favors the formation of isolated centers, and they are subsequently detected and investigated with great sensitivity using the μSR (muon spin rotation/relaxation/resonance) techniques. Similar to H, isolated Mu can be singly charged (positive or negative) or neutral in semiconductors. The neutral (paramagnetic) centers are characterized primarily by the electron hyperfine interactions with the muon and neighboring nuclear spins. Similar information on singly charged muonium centers can be obtained from the smaller muon-nuclear dipolar and muon-induced electric quadrupolar interactions with the neighboring nuclear spins.[1,2]

The most detailed structural information exists for muonium in GaAs, where both the neutral and charged muonium centers have been characterized. In semi-insulating (SI) GaAs at low temperatures two very distinct neutral centers are observed. Mu^0_{BC} is located at the bond center and is characterized by a small anisotropic muon-electron hyperfine interaction with most of the electron spin density residing on the two nearest neighbor Ga and As atoms.[3] Mu^0_T, on the other hand, has a large isotropic muon-electron hyperfine interaction about one-half that of muonium in vacuum.[1] The localized nature of the spin density and their stability with respect to temperature implies the energy levels for both Mu^0_{BC} and Mu^0_T fall deep within the gap, at least a few hundred meV below the conduction band. In heavily doped GaAs a singly charged muonium center is observed instead of the neutral paramagnetic centers. In *p*-type material a muon precession frequency close to the free Larmor precession is attributed to Mu^+ close to the bond center.[4,5] In *n*-type material the signal is attributed to Mu^- at the tetrahedral interstitial site with four nearest neighbor Ga nuclei.[6] Although the precession frequencies and nuclear dipolar linewidths (in low field) are very similar for Mu^- and Mu^+ the two centers are distinguished by the muon-induced quadrupolar interactions with the nearest neighbor nuclei. This leads to a distinct spectrum of muon-nuclear level crossing resonances (μLCR's) where cross relaxation is enhanced. In addition, the nuclear dipolar line broadening of the precession frequency has a distinct dependence on magnetic field as a result of the muon-induced nuclear quadrupolar interaction.

Much less is known about how the various muonium centers are formed in GaAs, or any other semiconductor, after the energetic muon is implanted. Information on this process is limited since it occurs on a short time scale immediately after implantation. Thus typically only the end products are observed. It is known, however, that in order to observe coherent precession signals in a μSR experiment muonium must be formed in a time much less than the hyperfine period (typically several ns for Mu^0_{BC} or 0.5 ns for Mu^0_T); otherwise considerable dephasing of the signal would occur. Recently, it has been shown that rather moderate electric fields of only 5–20 kV/cm can dramatically alter the muonium precession amplitudes.[7–11] In particular in GaAs it was found that the amplitude of a singly charged, i.e., diamagnetic, center (e.g., Mu^- or Mu^+) is enhanced at the expense of the neutral Mu^0_{BC} center.[7,10] Since epithermal processes are unlikely to be affected by such small electric fields this is evidence that Mu^0_{BC} is formed after the thermalization via capture of an electron from the radiation track left by the incoming muon. The strength of the required electric field is too small to directly field ionize the ground state of Mu^0_{BC}. Instead, the magnitude is more typical of that required to field ionize a shallow center or an exciton. One model which has been proposed is that the formation proceeds through an intermediate excited shallow muonium center.[7,9] If the electric field is sufficient to field ionize this intermediate state, then the capture of the electron into the ground state is inhibited, leading to an enhanced precession signal corresponding to Mu^+. A third body, either a second electron or hole from the radiation track, would be needed to carry away the excess momentum and energy on such a short time scale. It may also be possible that the formation occurs by capture into the ground state from an exciton with the hole carrying away the excess momentum and energy. In this case the effect of the electric field is to field ionize the exciton which then inhibits the electron capture by the muon since there is no third body to carry away energy and momentum. In either case the electric field acts to prevent the formation of muonium. Other possible explanations of the electric field dependence might also be considered. For example, if Mu^0_{BC} is formed epithermally it might be converted to either Mu^+ via capture of a thermalized hole or to Mu^- via capture of a second electron. In this case the role of the electric field might be to ionize excitons from the radiation track, thereby providing a source of free holes and electrons. Clearly it is important to verify that the state which is enhanced by the electric field is in fact Mu^+ at the bond center rather than Mu^- or Mu^+ at some other metastable site. A convincing identification of this center would help improve our understanding of muonium formation processes, and would help one to evaluate the extent to which electric fields can be used to control the resultant charge and site of Mu. There may also be a broader relevance since similar processes likely occur when any ion is implanted in a semiconductor.

In this paper we present spectroscopic evidence confirming that the state enhanced by an electric field in SI-GaAs at 10 K is the same center observed in *p*-type GaAs, attributed to isolated Mu^+ at the bond center. The nuclear dipolar linewidth of the precession frequency at 1 T agrees with that of Mu^+ for all electric fields in the ≈1–15 kV/cm range and is much larger than that seen previously for Mu^-. This assignment is confirmed by a muon-nuclear level crossing resonance at 20 kV/cm which clearly establishes that the observed center has the same muon induced Ga quadrupolar interaction as isolated Mu^+.

The transverse-field (TF) muon spin rotation and muon-level crossing resonance (μLCR) experiments were carried out on the M20B and M15 surface muon channels, respectively, at TRIUMF. Positively charged muons with ≈100% polarization and energy ≈4 MeV were injected into the sample. The majority of the data reported in this paper were obtained at 10 K on a high resistivity semi-insulating GaAs wafer from American Xtal Technology with dimensions 30 mm × 20 mm × 0.35 mm. The sample was oriented with a ⟨100⟩ axis parallel to the incoming muon beam and the applied magnetic field **B**. Silver of ≈1 μm was evaporated on both sides of the GaAs wafer. These silver layers served as electrodes for the application of the electric field. In order to prevent charge accumulation on the surface which reduces the electric field within the sample, **E** was alternated periodically between pointing either parallel or antiparallel to the incoming μ^+ direction.[10] A switching frequency of 10 Hz was used, which is well above that required to saturate the **E**-field enhanced signal in SI-GaAs.[10]

TF-μSR and μLCR data were collected for both electric field directions. In the TF-μSR part of the experiment, the incoming muon spin was rotated such that it was perpendicular to the applied magnetic field. Four positron counters were positioned around the sample in order to monitor the muon precession signal close to the free Larmor frequency of the muon ($\omega_\mu = \gamma_\mu B$ with a muon gyromagnetic ratio $\gamma_\mu = 2\pi \times 135.54$ MHz/T). In the μLCR measurements positron counters were placed forward and backward with respect to the incoming muon spin and the time-integrated count rates recorded for each counter. In order to reduce the undesirable effects due to beam fluctuations, an additional modulation field was applied along the main field direction. This additional field was flipped between ≈+2 mT and ≈−2 mT every few seconds and the normalized difference in the integrated count rates at these two magnetic fields recorded. A muon level crossing resonance therefore appears as a derivativelike line shape.

We first discuss the TF-μSR data. In principle there is a site dependent chemical shift[12] but this is too small to measure with sufficient accuracy to distinguish Mu^- from Mu^+. However, the relaxation of the precession signal can be used. This damping, or dipolar linewidth, is attributed to a spread in the internal field distribution arising from the randomly oriented host nuclear moments. The damping rate varies with the applied magnetic field. (This is also referred to as a Hartmann curve.[13]) Previous measurements of isolated Mu^+ and Mu^- in heavily doped GaAs with $E=0$ have shown that a Gaussian of the form $\exp(-\sigma^2 t^2)$ provides a very good phenomenological description of the depolarization of the precession signal.[2,5,6,14] Furthermore, as the magnetic field is increased, prominent drops in σ will occur for both isolated Mu^+ and Mu^- when **B** is applied parallel to a ⟨100⟩ axis.[5,6] (Note that both centers are static at 10 K). The crossover B_{cr} between the low field and high field values of σ occurs when the muon-induced quadrupolar interaction on a nearest neighbor host nucleus is comparable to $\gamma_N B_{cr}$ (where γ_N is the gyromagnetic ratio of the nucleus). The values of B_{cr} are very different for Mu^+ and Mu^-. These observations are summarized in Fig. 1 which shows a reproduction of the Hartmann curves for isolated Mu^+ and Mu^- in heavily doped GaAs.[5,6] Coincidentally, the values of σ for Mu^+ and Mu^- are very similar at low magnetic fields (<100 mT), i.e.,

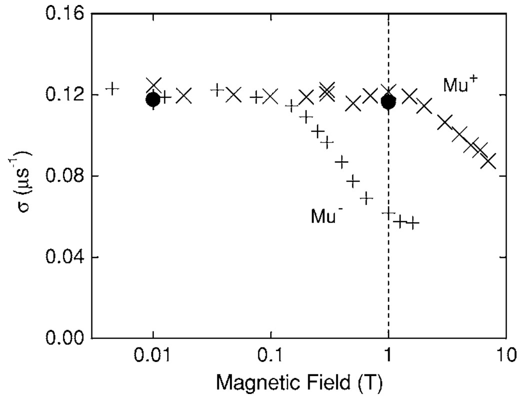

FIG. 1. Relaxation of the transverse field diamagnetic signal at various magnetic fields. The ×'s and +'s correspond to σ values for Mu^+ and Mu^-, respectively. The circles are experimental values collected with $E=14.3$ kV/cm. The vertical dashed line is located at $B=1$ T, where the transverse field experiments in this paper were performed.

$\approx 0.12\ \mu s^{-1}$. However, for a magnetic field of 1 Tesla, the relaxation for Mu^+ remains close to the low field value, but the value for Mu^- drops[6] to $\sim 0.06\ \mu s^{-1}$. Hence, by measuring σ of the **E**-enhanced diamagnetic state at 1 T, we can exploit this difference to identify whether it is Mu^+ or Mu^-. This is illustrated in Fig. 1 with $E=14.3$ kV/cm (circles) applied to our GaAs wafer, showing that at this particular electric field, the relaxation is consistent with that expected for isolated Mu^+ and very different than for Mu^-.

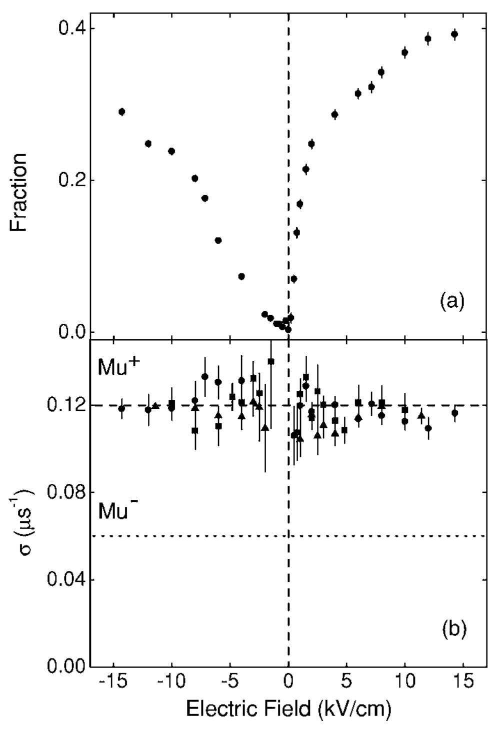

FIG. 2. (a) The electric field dependence of the fraction of implanted muons that end up diamagnetic in one of the SI-GaAs samples. $E>0$ corresponds to the electric field direction applied parallel to the incoming muon momentum. (b) Relaxation of the transverse field precession diamagnetic signal at various applied electric fields. The different symbols correspond to different SI-GaAs samples. The dashed and dotted lines indicate the known experimental values for isolated Mu^+ and Mu^-, respectively.

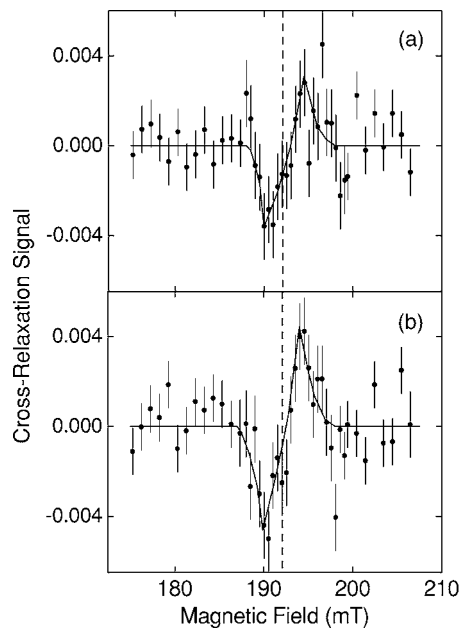

FIG. 3. μLCR spectra for SI-GaAs, with $\mathbf{B}\|\langle 100\rangle$ and $E=20$ kV/cm. (a) μLCR data for **E** opposite to incoming muon momentum. (b) μLCR data for **E** parallel to incoming muon momentum. In (a) and (b), the solid line is a guide to the eye. The vertical dashed line indicates the position of the Ga-μ^+ resonance from previous measurements (see text).

Figure 2(a) shows the **E** dependence of the fractional amplitude of the diamagnetic signal in our GaAs wafer with $B=1$ Tesla applied parallel to a $\langle 100\rangle$ direction. The behavior is typical for GaAs subjected to electric fields.[10] At $E=0$, there is a very small diamagnetic signal and as the electric field is increased, the fraction increases asymmetrically about $E=0$. Figure 2(b) shows the electric field dependence of the experimentally measured relaxation rate σ of the diamagnetic state in the same GaAs sample as well as in two other $\langle 100\rangle$ semi-insulating GaAs samples from American Xtal Technologies. Comparison with the known relaxation rates for Mu^+ and Mu^- clearly indicates that at electric fields from ≈ 1 to 15 kV/cm, the **E**- enhanced diamagnetic state is not Mu^-. On the other hand, the data are consistent with that expected for Mu^+. (Note that for smaller values of the electric field the diamagnetic fraction is extremely small, making it difficult to extract statistically reliable information on σ and the charge state for $E<1$ kV/cm.) Furthermore, there is no detectable change in the phase shift of the precession signal as a function of the electric field (not shown). This result is consistent with the diamagnetic state being the initial state of the **E**-enhancement process rather than a final state.

We now describe the muon level-crossing resonance data of the **E**-enhanced signal. These resonances are very small and are only detectable if the diamagnetic fraction is large. Hence, they were only carried out at a high electric field. Such resonances occur when the energy splitting of the muon and a neighboring nucleus match, allowing the two species to transfer polarization between each other. A decrease in the muon polarization is observed at the magnetic field where such a condition is satisfied, as determined primarily by the muon-induced quadrupole interaction on the neighbor. Previous measurements in heavily doped GaAs with $E=0$ have established that isolated Mu^+ and Mu^- are characterized by very different resonances. In the case of Mu^+, with $\mathbf{B}\parallel\langle 100\rangle$, resonances due to both Ga and As have been observed and occur at magnetic fields greater than 180 mT.[4] On the other hand, resonances associated with Mu^- occur below $\approx$50 mT.[6]

Figure 3 shows the data from our current μLCR experiments on the **E**-enhanced diamagnetic state, carried out at $E=20$ kV/cm. In both electric field directions, a resonance is observed at $\approx$192 mT. From comparison with previous experiments, the location of this resonance can be unambiguously identified with a neighboring ^{71}Ga of isolated Mu^+. The sizes of the signals are obtained by normalizing to the size of the TF-μSR diamagnetic signals at $E=\pm 20$ kV/cm, and can be compared to the size of the μLCR signal in p-type GaAs of $\approx$0.0035.[4] Hence, within error, all of the diamagnetic fraction is accounted for in both electric field directions. Therefore, the μLCR data demonstrate that the **E**-enhanced diamagnetic state at this electric field is isolated Mu^+.

Thus both the TF-μSR and μ-LCR measurements at 10 K indicate that the electric field leads to an enhanced signal for isolated Mu^+ in SI-GaAs. This is true for all magnitudes of the electric field in the range $\approx$1–15 kV/cm and for either direction. This rules out any model in which the electric field leads to formation of Mu^-, at least at 10 K. We also find no detectable phase shift in the precession signal as a function of electric field. This is consistent with the observed signal being the initial state of the process rather than a final state. Hence, these data are consistent with a model in which the electric field acts to prevent the formation of Mu_{BC}^0 through capture of a thermalized electron produced in the radiation track of the muon.[7,9]

The research in this paper, and TRIUMF, are partially supported by the National Sciences and Engineering Research Council of Canada. One of the authors (R.L.L.) is supported by the US National Science Foundation (Grant No. DMR-102862) and Robert A. Welch Foundation (Grant No. D-1321). The authors would like to thank K.L Hoffman, W.A. MacFarlane, and A.N. MacDonald for experimental assistance. In addition, the authors acknowledge J.H. Brewer, D.G. Eshchenko, and V.G. Storchak for their assistance in the initial development of the EF-μLCR technique.[15]

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