Muonium Formation via Electron Transport in Silicon

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We report muon spin rotation measurements in n-type silicon from 10 to 310 K in electric fields up to 5 kV/cm. These experiments reveal the nature of the partition of neutral muonium centers into *normal muonium* (Mu_T^0) and *anomalous muonium* ($\mathrm{Mu}_{\mathrm{BC}}^0$): Formation of Mu_T^0 is consistent with *epithermal* processes prior to thermalization, while $\mathrm{Mu}_{\mathrm{BC}}^0$ is formed via electron transport to a *thermalized* positive muon. The spatial distribution of the excess electrons created in the μ^+ ionization track is shown to be anisotropic with respect to the muon. [S0031-9007(97)02788-9]

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Muonium (Mu) is a hydrogenlike atom with a positive muon (μ^+) as its nucleus, commonly formed when initially energetic muons are implanted in insulators or semiconductors [1]. It behaves in all respects as an isotope of hydrogen and, thanks to the sensitivity with which it may be detected and its hyperfine parameters determined by means of muon spin rotation spectroscopy or μ^+SR [1], provides an invaluable model for hydrogen in materials where hydrogen itself is difficult to detect by conventional spectroscopies. Semiconductors are a case in point: The electronic structure and dynamics of hydrogen in semiconductors are of fundamental interest and technological importance primarily because, even as a trace impurity, they can profoundly modify electronic properties [2,3]. Yet surprisingly little is known about isolated hydrogen defect centers and it is here that μ^+SR studies of their muonium counterparts have provided unique insights [4,5].

There are, however, important differences between the ways in which the two hydrogen isotopes—protium and muonium—are introduced into the sample and subsequently detected. Hydrogen, i.e., protium, is introduced chemically (whether deliberately or inadvertently) during the sample preparation and has ample time to reach thermodynamic equilibrium and to seek out and pair with other impurities or defects before detection. Muonium, by contrast, is formed during or immediately following high energy μ^+ implantation [8], and only those states reached on the microsecond time scale of the muon lifetime can be studied. The relevant question is how far one may stretch the analogy between hydrogen and muonium in order to model hydrogen behavior in matter.

The incoming μ^+ leaves behind an ionization track whose radiolysis products may subsequently interact with the muon. It has been customary to assert [6] that in solids the μ^+ thermalizes far enough from its own last ionization products that such complications are unimportant. However, some of the excess electrons generated in the μ^+ track may be mobile enough to reach the thermalized muons. Subsequent capture of a radiolytic electron has long been recognized as a possible route to muonium formation [7]. Recent experiments in *insulators* [8–11] convincingly showed that Mu atoms are sometimes formed via transport of excess electrons to positive muons. (In superfluid helium it is formed mainly via *muon* transport [12].) In this Letter we present experimental evidence that this mechanism can also prevail in a *semiconductor*, namely, silicon.

In silicon at low temperatures, two quite different neutral centers are formed, namely, Mu_T^0 (located in the tetrahedral interstitial site and formerly denoted *normal muonium* or Mu) and $\mathrm{Mu}_{\mathrm{BC}}^0$ (located at the center of an expanded Si-Si bond and known also as *anomalous muonium* or Mu^*) [4]. Both are paramagnetic but lose the unpaired electron to the conduction band at high temperature. Ionization begins near 150 K for $\mathrm{Mu}_{\mathrm{BC}}^0$ although the muon polarization from this fraction is only fully recovered in the Larmor precession signal of electronically diamagnetic muons at 220 K [4]; the intermediate region around 200 K provides favorable conditions for the present experiment. The onset of ionization is about room temperature for Mu_T^0.

Until now, the nature of the partition of muons implanted into semiconductors between Mu_T^0 and $\mathrm{Mu}_{\mathrm{BC}}^0$ has been something of a puzzle. The so-called "spur model" [7], although hotly debated in the context of muonium formation in insulating and molecular materials, has not received much attention for the particular case of semiconductors, and the notion of a charge-exchange cycle at the epithermal stage [6] has scarcely been challenged. It seems appropriate to question this long-standing assumption, especially in light of recent theoretical considerations for charged diamagnetic species in silicon, where the site preferences are found to be much more pronounced than for the neutral atoms [3]. Thus the positive ion is predicted to exist only as $\mathrm{Mu_{BC}}^+$ (i.e., at the bond-center site) and the negative ion only as Mu_T^- (at the cage-center). Since Mu_T^+ is energetically unfavorable, one can hardly expect it to be a center for delayed Mu_T^0 formation via excess electron transport; by contrast, $\mathrm{Mu_{BC}}^+$, being relatively stable, would certainly seem to be a candidate. These facts imply that the two neutral muonium centers in silicon could well be formed via different channels. In this Letter we present experimental evidence in favor of *delayed* formation of $\mathrm{Mu}_{\mathrm{BC}}^0$ via excess electron transport to $\mathrm{Mu_{BC}}^+$ while supporting the model of epithermal formation for Mu_T^0.

The present experiments were performed on the surface muon beam lines EMU of the ISIS Pulsed Muon Facility at the Rutherford Appleton Laboratory and M13 at TRIUMF. The silicon sample used in these experiments was a lightly doped n type with a nominal resistivity of 6000 Ω cm at room temperature, from which we estimate the dopant level to be no more than $10^{13}\ \mathrm{cm}^{-3}$.

Both surfaces of a square sample 1.2×1.2 cm with a thickness of 300 μm (a fully depleted silicon detector) were covered with 1 μm thick layers of aluminum electrodes to produce an electric field parallel or antiparallel to the initial muon momentum. At both laboratories, positive muons of 28 MeV$/c$ momentum and 100% spin polarization were stopped in the silicon and μ^+SR spectra recorded at various different temperatures and applied electric and magnetic fields.

At ISIS, the pulsed structure of the muon beam precludes detection of transverse-field $\mathrm{Mu}_{\mathrm{BC}}^0$ precession signals; in a low transverse magnetic field ($H = 2$ Oe, which is low enough that the splitting of the Mu_T^0 precession frequency could be ignored), the Mu_T^0 and diamagnetic (D) signals are observed with an overall time dependence,

$$A_0 P(t) = \frac{A_{\mathrm{Mu}_T}}{2} \exp(-\lambda_{\mathrm{Mu}_T} t) \cos(\omega_{\mathrm{Mu}_T} t + \varphi) + A_{\mathrm{D}} \exp(-\lambda_{\mathrm{D}} t) \cos(\omega_\mu t + \varphi_{\mathrm{D}})\,. \quad (1)$$

Here A_0 is a normalization factor (the maximum muon decay asymmetry); $\omega_{\mathrm{Mu}_T} = \gamma_{\mathrm{Mu}_T} H$ and $\omega_\mu = \gamma_\mu H$, where $\gamma_{\mathrm{Mu}_T}/2\pi = 1.3945$ MHz/Oe and $\gamma_\mu/2\pi = 13.553$ kHz/Oe are the muonium and μ^+ magnetogyric ratios; A_{Mu_T} and A_{D} are the muonium and diamagnetic asymmetries (proportional to the corresponding ensemble fractions); and λ_{Mu_T} and λ_{D} are the corresponding relaxation rates. Note that $P(0) < 1$ due to the unobserved high-frequency components. At higher magnetic fields (e.g., $H = 80$ Oe) the Mu_T^0 signal likewise becomes invisible, so that in this case the muon polarization is described by Eq. (1) with A_{Mu_T} set to zero. Figure 1 presents the temperature dependence of the diamagnetic asymmetry extracted from Eq. (1).

We attribute the increase in the diamagnetic amplitude beginning above 150 K to ionization of $\mathrm{Mu}_{\mathrm{BC}}^0$, yielding the positively charged center $\mathrm{Mu_{BC}}^+$. Only for much more heavily doped samples, or at lower temperatures, does the negative ion (Mu_T^-) appear to play a significant role in muonium state dynamics [13,14].

At TRIUMF, the continuous time structure of the μ^+ beam permits the simultaneous observation of the $\mathrm{Mu}_{\mathrm{BC}}^0$, Mu_T^0, and diamagnetic signals in the same silicon sample in a transverse magnetic field of 64 Oe. All three signals were therefore taken into account in fitting experimental time spectra of the muon polarization. The ionization of $\mathrm{Mu}_{\mathrm{BC}}^0$ leads to the disappearance of the corresponding signals above 150 K. The two spectral lines of Mu_T^0 (the triplet precession frequency is split [6] in the higher fields used at TRIUMF) were independent of temperature over the whole temperature range studied with an asymmetry corresponding to about 40% of the total polarization. The temperature dependence of the diamagnetic asymmetry obtained at TRIUMF was qualitatively the same as that obtained at ISIS (see Fig. 1) although reduced by a temperature independent multiplicative factor of about 0.7. The larger value at ISIS probably represents muons stopped outside the sample (the possibilities for beam collimation close to the sample being limited at a pulsed

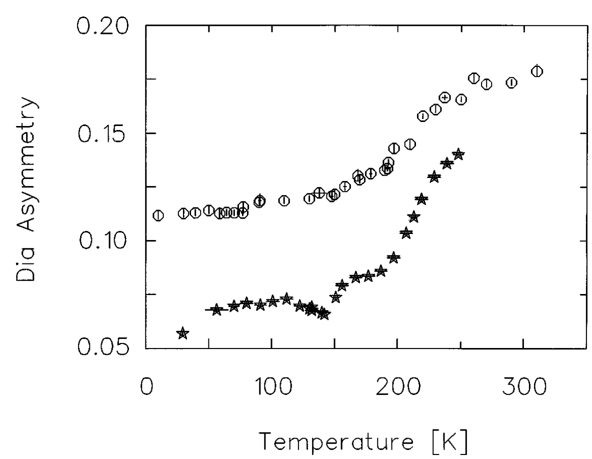

FIG. 1. Temperature dependence of the diamagnetic amplitude in a lightly doped n-type silicon sample in transverse magnetic fields of $H = 80$ Oe (circles, ISIS data) and $H = 64$ Oe (stars, TRIUMF data).

source). At TRIUMF, collimation of the muon beam to 10 mm considerably reduced the background signal.

Application of electric fields to the sample at 202 K reveals a strong dependence of the diamagnetic asymmetry on the strength and direction of the applied field, as shown in Fig. 2. Here positive and negative E correspond, respectively, to the external electric field applied parallel and antiparallel to the initial μ^+ momentum direction: Assuming that the muons thermalize (on average) downstream of their final radiolysis products, positive E therefore pulls the μ^+ and e^- apart, whereas negative E pushes the μ^+ and e^- together.

Any increase of the diamagnetic fraction with electric field is expected to be at the expense of the paramagnetic fraction(s), yet our data at $T = 202$ K show the Mu_T^0 fraction to be unaffected by application of E (to within an experimental uncertainty which is an order of magnitude less than its expected change). Since the change in the diamagnetic fraction with E is *not* at the expense of the Mu_T^0 fraction, the Mu_T^0 state must indeed be formed promptly, and there is no reason to doubt that this occurs at the *epithermal* stage. Further support for the epithermal model comes from the fact that A_{Mu_T} is found to be temperature independent. The alternative process, namely, *delayed* muonium formation via charge transport, involves *thermalized* particles and is inevitably temperature dependent through the electron mobility [8,9]. We therefore conclude that the increase of the diamagnetic fraction with electric field takes place at the expense of the $\mathrm{Mu}_{\mathrm{BC}}^0$ fraction and infer that $\mathrm{Mu}_{\mathrm{BC}}^0$ must be formed thermally by transport of radiolysis electrons from the muon's ionization track to the μ^+. Since the $\mathrm{Mu}_{\mathrm{BC}}^0$ signal is not detected, either the electron transport takes longer than the typical period of μ^+ polarization oscillations in $\mathrm{Mu}_{\mathrm{BC}}^0$ or the characteristic time for subsequent thermal ionization of $\mathrm{Mu}_{\mathrm{BC}}^0$ is too short to permit its observation. At this temperature (202 K) the absence of a detectable $\mathrm{Mu}_{\mathrm{BC}}^0$ signal is probably due to its rapid ionization.

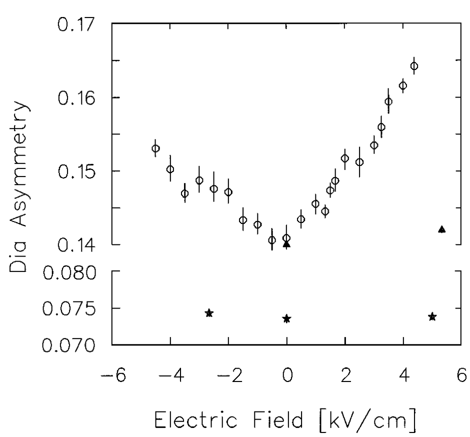

FIG. 2. Electric field dependence of the diamagnetic amplitude in silicon at $T = 202$ K (circles, ISIS data), $T = 151$ K (stars, TRIUMF data), and $T = 250$ K (triangles, TRIUMF data).

Experiments at lower temperatures—141 K at ISIS and 120 and 151 K at TRIUMF—revealed *no* electric field dependence of the diamagnetic fraction; that is, the effect is negligible at all temperatures where the $\mathrm{Mu}_{\mathrm{BC}}^0$ signals are detectable. This could be due to a reduction in the characteristic muon-electron distance at lower T, increasing the muon-electron Coulomb attraction until it cannot be overcome by an externally applied electric field. The effect also disappears at higher temperature ($T = 250$ K): Ionization is so fast at this temperature that any time spent as $\mathrm{Mu}_{\mathrm{BC}}^0$ is a negligible fraction of a hyperfine period and has almost no effect on the μ^+ polarization in the diamagnetic signal.

Since our model for delayed formation of $\mathrm{Mu}_{\mathrm{BC}}^0$ relies on measurements made in the narrow temperature regime between the onset of $\mathrm{Mu}_{\mathrm{BC}}^0$ ionization and the recovery of the $\mathrm{Mu}_{\mathrm{BC}}{}^+$ signal in the transverse-field spectra, it must be set against other possibilities, e.g., the electric field in some sense *assisting* the ionization. This latter possibility may reasonably be dismissed, since we find a small but significant *anisotropy* in the influence of the electric field: In Fig. 2 the typical slope of the E dependence for positive E may be seen to be steeper than that for negative E. This, in turn, is the signature of an anisotropy in the spatial distribution of the muons relative to the excess electrons, confirming that muons do indeed thermalize "downstream" from the "center" of the excess electron distribution. A similar anisotropy has been seen in liquid helium [15]. In solid nitrogen [9] and liquid neon [11], experiments also show anisotropic spatial distributions of the electrons with respect to the μ^+, but the electric field dependence is qualitatively different: While the diamagnetic fraction f_{D} increases and the muonium fraction f_{Mu} decreases with positive E, as in liquid helium and in silicon, the application of *negative* E actually *decreases* f_{D} and, accordingly, *increases* f_{Mu}. This behavior may be explained by a peculiar electron delocalization process in a high electric field [16] combined with the anisotropic spatial distribution of the free electrons [17]. However, a detailed model for the manifestations of such an anisotropy is beyond the scope of this paper; its mere existence is sufficient for our present arguments.

These findings are relevant to the use of muonium spectroscopy for modeling hydrogen in semiconductors. It is important to establish that the process of muon implantation does not create muonium states which are somehow different from those of protium or inaccessible through normal thermal processes. In fact, the bond-centered state is now understood to be the ground state for interstitial hydrogen in silicon: The so-called AA9 center, which in the new notation we would denote as H_{BC}^0, has been detected by ESR spectroscopy [18]. It may also be that the capture of radiolytic electrons by protons has some role to play in the performance of semiconductor devices subjected to ionizing radiation.

In conclusion, we have demonstrated the influence of an external electric field on the initial partition of muon states in silicon. There is no reason to question the epithermal model for Mu_T^0 formation, but we argue that $\mathrm{Mu}_{\mathrm{BC}}^0$ is formed via electron transport to ${\mathrm{Mu}_{\mathrm{BC}}}^+$, i.e., via a two-stage process in which the μ^+ is initially thermalized at the bond-center site and subsequently captures a radiolytic electron. The spatial distribution of such electrons with respect to the μ^+ is shown to be anisotropic, consistent with muon thermalization downstream from the center of the excess electron distribution.

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[1] A. Schenck, *Muon Spin Rotation: Principles and Applications in Solid State Physics* (Adam Hilger, Bristol, 1986); S. F. J. Cox, J. Phys. C **20**, 3187 (1987); J. H. Brewer, *Muon Spin Rotation/Relaxation/Resonance*, Encyclopedia of Applied Physics (VCH, New York, 1994), Vol. 11, p. 23.

[2] *Hydrogen in Semiconductors*, edited by J. Pankove and N. M. Johnson (Academic, New York, 1990).

[3] S. M. Myers *et al.*, Rev. Mod. Phys. **64**, 559 (1992).

[4] B. D. Patterson, Rev. Mod. Phys. **60**, 69 (1988).

[5] T. L. Estle and R. L. Lichti, Hyperfine Interact. **97**/**98**, 171 (1996).

[6] J. H. Brewer, K. M. Crowe, F. N. Gygax, and A. Schenck, in *Positive Muons and Muonium in Matter*, edited by V. W. Hughes and C. S. Wu, Muon Physics (Academic Press, New York, 1975), Vol. III, pp. 3–139.

[7] P. W. Percival, E. Roduner, and H. Fischer, Chem. Phys. **32**, 353 (1978).

[8] V. Storchak, J. H. Brewer, and G. D. Morris, Phys. Lett. A **193**, 199 (1994).

[9] V. Storchak, J. H. Brewer, and G. D. Morris, Phys. Rev. Lett. **75**, 2384 (1995).

[10] V. Storchak, J. H. Brewer, and G. D. Morris, Philos. Mag. **72**, 241 (1995).

[11] V. Storchak, J. H. Brewer, and G. D. Morris, Phys. Rev. Lett. **76**, 2969 (1996).

[12] E. Krasnoperov *et al.*, Phys. Rev. Lett. **69**, 1560 (1992).

[13] S. R. Kreitzman *et al.*, Phys. Rev. B **51**, 13 117 (1995).

[14] R. L. Lichti, Philos. Trans. R. Soc. A, Phys. Sci. Eng. **350**, 169 (1995).

[15] E. Krasnoperov *et al.*, Hyperfine Interact. **87**, 1011 (1994).

[16] Y. Sakai, W. F. Schmidt, and A. Khrapak, Chem. Phys. **164**, 139 (1992).

[17] D. G. Eshchenko (private communication).

[18] Yu. V. Gorelkinskii and N. N. Nevinnyi, Sov. Tech. Phys. Lett. **13**, 45 (1987).