PHYSICAL REVIEW B VOLUME 55, NUMBER 7 15 FEBRUARY 1997-I

Evidence for muonium passivation in *n*-doped Ge

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(Received 28 October 1996)

Two different diamagnetic muon states have been identified through their response to bulk electronic excitation in crystalline *n*-type Ge: one, found above ~100 K, rapidly charge exchanges with photogenerated carriers, while the other, seen at low temperatures, shows little or no such behavior. The electronic inactivity of the latter state (Mu^-, produced by a slow charge-transfer reaction between muonium and an impurity donor atom) further suggests that the electronic level is located outside the energy-band gap, equivalent to ''muonium passivation'' of the donor. [S0163-1829(97)09207-2]

Electronic excitation processes in nonmetallic materials have recently become a topic of intensive study. Excitation can be a means of creating hitherto unknown metastable states which may serve as potential channels (reactive intermediates) in the synthesis of materials, or be useful in other applications. In particular, it is well known that in semiconductors and ionic crystals bulk excitation leads to temporary changes in the local electronic structure at sites such as defect centers, in some cases resulting in local atomic migration. In recent experiments we found evidence of migration of muonium centers (muonium, Mu, is an analog of atomic hydrogen in which the proton is replaced by a positive muon) in crystalline silicon between the tetrahedral interstitial site ($\mathrm{Mu}_T{}^0$) and Si-Si bond center site ($\mathrm{Mu}_{\mathrm{BC}}{}^0$) induced by photoexcitation.[1] The details of the process involved in this muonium transition are the subject of continuing investigation.

The current state of knowledge about the dynamical properties of atomic defects under thermal and/or electronic excitations (including defect metastability and associated site change) in semiconductors is still rather limited compared with the situation regarding their equilibrium structure. In this regard, hydrogen isotopes are no exception, despite their apparent simplicity; the accumulated knowledge largely relates to the electronic structure of isolated (paramagnetic) muonium centers, for which high-resolution μSR (muon spin rotation, relaxation, and resonance) (Ref. 2) spectroscopic techniques analogous to electron paramagnetic resonance and electron-nuclear double resonance are available. The situation is more difficult where the study of diamagnetic muon states (μ_d, i.e., μ^+ or Mu^-) is concerned, as such high-resolution spectroscopy is not possible due to the absence of the electron-muon hyperfine interaction. Fortunately, there have been some attempts in recent years to address the defect dynamics through study of the muonium centers in crystalline Si under photoexcitation[1,3] or at high temperatures.[4,5]

In this paper we show that charge-exchange–spin-exchange interaction between implanted muons and excess carriers may serve as a probe of the electronic state of diamagnetic muons in semiconductors. We found that a μ_d state slowly formed at lower temperatures in *n*-Ge does not interact with photoinduced excess carriers, suggesting that the electronic level associated with the μ_d state is not in the band gap. Since the μ_d state seems to be Mu^- formed by a process $\mathrm{Mu}_T{}^0+d^0\rightarrow\mathrm{Mu}_T{}^-d^+$, the result is strong evidence that the observations correspond to the passivation of donor levels by $\mathrm{Mu}_T{}^0$ centers, a phenomenon of crucial importance in determining the electronic transport properties of semiconductors.[6] A second μ_d state, observed above ~100 K, undergoes rapid cyclic charge exchange reaction with excess carriers,[1] strongly suggesting that it is the ionized state of the bond center muonium $\mathrm{Mu}_{\mathrm{BC}}{}^+$, with its associated electronic level in the band gap as predicted by theory.

The experiment was conducted primarily at the RIKEN-RAL Muon Facility in the Rutherford Appleton Laboratory, which provided a pulsed (70-ns width, 50-Hz repetition) beam of nearly 100% spin-polarized muons with a momentum of 27 MeV/c. A part of the measurement was performed at the Meson Science Laboratory, University of Tokyo (UTMSL, located at National Laboratory for High Energy Physics, Tsukuba). The single-crystal Ge specimen described in Ref. 1 (subsequently discovered to be *n*-doped with Sb, with $[\mathrm{Sb}]\sim10^{14}$ cm^{-3} estimated from $\rho\sim15\ \Omega$ cm) was used again in the current experiment. The experimental apparatus is similar to that previously used,[1] except that a flashlamp with higher light intensity was adopted for the RAL experiment. The time-differential μSR spectra were measured under alternate switching of illumination between ''on'' (flash) and ''off'' (no-flash) states at every muon beam pulse, with data sorted into two independent histograms by a front-end processor to minimize systematic error from muon beam fluctuation.

It is known from earlier experiments that the μ_d state observed above 100 K is formed quasipromptly from a para-

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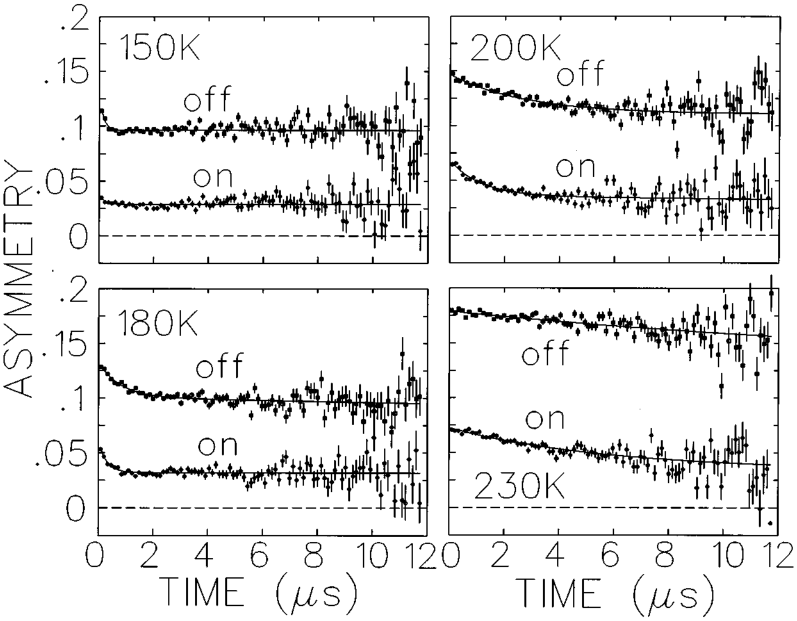

FIG. 1. Time spectra of decay positron asymmetry in n-Ge with (''on'') and without (''off'') illumination at various temperatures under LF $=0.01$ T. Note that there are two components, one corresponding to an immediate reduction of asymmetry upon illumination, and another slowly relaxing with a slightly increased relaxation rate under illumination.

magnetic precursor (probably $\mathrm{Mu}_T{}^0$) with a temperature dependent transition rate $\Lambda(T)=T^{1/2}\Lambda_0\exp(-E_a/kT)$ with an activation energy $E_a=0.184(7)$ eV.[7] In the ''dark'' (unilluminated) specimen, as the temperature is raised, the transition rate approaches the hyperfine frequency ω_0 of $\mathrm{Mu}_T{}^0$ centers (e.g., $\Lambda\sim7\times10^8$ s^{-1} at 200 K, while $\omega_0/2\pi=2.359\times10^9$ s^{-1}), leading to a recovery of muon polarization. Figure 1 shows the time spectra under longitudinal field (LF$=0.01$ T) obtained with and without illumination above 100 K, where significant reduction of μ-e decay asymmetry is seen upon illumination; note that a decay asymmetry of ~0.2 corresponds to 100% muon polarization. The amount of reduction corresponds to the asymmetry of the quasiprompt μ_d state, and indicates that the polarization of the μ_d state is lost by illumination within $\delta\sim70$ ns (i.e., the muon beam pulse width). Such fast polarization loss is attributed to cyclic charge exchange with photoinduced carriers. The depolarization rate corresponds to the charge exchange rate ν at this LF range,[8] and thus Fig. 1 indicates that $\nu\gg\delta^{-1}\sim10^7$ s^{-1}. An excitation spectrum obtained using band-pass filters shows a Gaussian-like peak of photoinduced relaxation of μ_d at 0.72 eV with a full width at half maximum of 0.15 eV, indicating that interaction with excess carriers generated by bulk excitation near the band-gap energy (0.67 eV) is predominant. The excess carrier density n_p estimated from the measured photon influx was about 10^{15} cm^{-3}. The cross section for the μ_d carrier interaction is then estimated to be $\sigma\simeq\nu/(n_p v)\gtrsim10^{-15}$ cm^2, which is typical (if $v\simeq10^7$ cm/s is a typical Fermi velocity).

On the other hand, a more interesting aspect of these spectra is that there is another component which exhibits moderate depolarization only weakly affected by illumination. The yield of quasiprompt μ_d decreases monotonically with decreasing temperature, and is negligibly small (less than 5%, corresponding asymmetry <0.01) below 10 K. However, as seen in Fig. 2(c) the time spectra under a low longitudinal field ($=0.01$ T) show an asymmetry reduction larger than that expected from the depolarization of the quasiprompt μ_d state alone. Moreover, the spectra in Fig. 2 consist of relaxing and nonrelaxing components with relative amplitudes dependent on the applied longitudinal field, a feature characteristic of slow irreversible conversion from a state undergoing spin-exchange–charge-exchange interaction to the final nonrelaxing state. The time evolution of the longitudinal polarization for the transition $\mathrm{Mu}_T{}^0\rightarrow\mu_d$ is given by

$$P_{T/d}(t,x)\simeq P^{(0)}_{T/d}(x)e^{-(\kappa+\lambda)t}+P^{(\infty)}_{T/d}(x), \tag{1}$$

$$P^{(0)}_{T/d}(x)\simeq\frac{(\nu/\kappa)(1+2x^2)}{(1+\nu/\kappa+x^2)(2+2x^2)}, \tag{2}$$

$$P^{(\infty)}_{T/d}(x)\simeq\frac{1+2x^2}{2+2\nu/\kappa+2x^2}, \tag{3}$$

$$\lambda=\nu/(1+x^2),$$

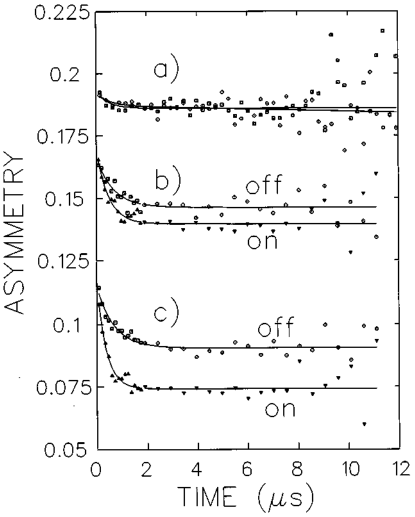

FIG. 2. Time spectra of decay positron asymmetry in Ge at 12 K with (''on'') and without (''off'') illumination with (a) LF$=0.34$, (b) 0.1, and (c) 0.01 T.

where ν is the spin-exchange–charge-exchange rate, $\kappa(\ll\omega_0)$ is the conversion rate, and $x=(\gamma_\mu-\gamma_e)B/\omega_0$ is the normalized external field (with γ_μ and γ_e being the respective muon and electron gyromagnetic ratio, and ω_0 the muonium hyperfine parameter).[2,9] The residual polarization $P^{(\infty)}_{T/d}(x)$ corresponds to the yield of the final diamagnetic state. It is then clear from Fig. 2 that the conversion process is weakly affected by illumination to reduce the final-state polarization, but that the final state itself is unaffected: otherwise the final-state polarization would necessarily have been completely lost under illumination. This is in marked contrast with the diamagnetic state seen at higher temperatures, where fast depolarization due to spin-exchange–charge-exchange interaction was observed under illumination.[1]

Further understanding of the process at low temperatures is obtained by an analysis of the detailed field dependences of the LF-μSR spectra (“repolarization patterns”). We found the time-dependent positron decay asymmetry in dark n-Ge to obey

$$A(t,x)=A_0P_z(t,x) \tag{4}$$

$$=A_0[f_{+/T}P_{+/T}(t,x)+f_{T/d}P_{T/d}(t,x)+f_TP_T(x)+f_{\mathrm{BC}}P_{\mathrm{BC}}(x)], \tag{5}$$

$$P_T(x)=(1+2x^2)/(2+2x^2), \tag{6}$$

where $A_0(\simeq 0.2)$ is the experimental asymmetry, f_α is the relative yield of respective states [with $\alpha=+/T$ and T/d corresponding to the states undergoing processes μ_d (prompt, probably $\mathrm{Mu}_T{}^+$)$\rightarrow\mathrm{Mu}_T{}^0$, $\mathrm{Mu}_T{}^0$ (prompt)$\rightarrow\mu_d$, and T and BC to stationary (nonreacting) $\mathrm{Mu}_T{}^0$ and $\mathrm{Mu}_{\mathrm{BC}}{}^0$ centers, overall satisfying $\Sigma_\alpha f_\alpha=1$], and $P_\alpha(t,x)$ is the corresponding polarization function. [For $P_{\mathrm{BC}}(x)$ see Ref. 10).] The first term describing slow $\mathrm{Mu}_T{}^0$ formation is necessary for a self-consistent analysis of the present data, and may be expanded as

$$P_{+/T}(t,x)=P^{(0)}_{+/T}(x)e^{-\kappa' t}+P^{(\infty)}_{+/T}(x) \tag{7}$$

$$=[e^{-\kappa' t}+(1+2x^2)]/(2+2x^2), \tag{8}$$

with κ' the $\mathrm{Mu}_T{}^0$ formation rate. Note that the field dependence of Eq. (7) is very different from Eq. (1), particularly at $t=0$, where Eq. (7) leads to unit polarization while $P^{(0)}_{T/d}(x)+P^{(\infty)}_{T/d}(x)=P_T(x)$ in Eq. (1). In addition, a fraction of $\mathrm{Mu}_T{}^0$ was found to remain intact irrespective of illumination, and is included as the third term in Eq. (5): we have confirmed in a recent experiment that the $\mathrm{Mu}_T{}^0$ state itself is not influenced by illumination.[11] Then the initial asymmetry $A(0,x)$ versus field [A in Fig. 3(a)] is well reproduced by assuming the presence of $\mathrm{Mu}_T{}^0(f_T+f_{T/d}\sim 0.7)$, $\mathrm{Mu}^0_{\mathrm{BC}}(f_{\mathrm{BC}}\sim 0.15)$, and a fraction which undergoes delayed ($\kappa'\sim 10^{-6}$ s) $\mathrm{Mu}_T{}^0$ formation ($f_{+/T}\sim 0.15$).

The residual asymmetry

$$A(\infty,x)=A_0P_z(\infty,x)=A_0[(f_{+/T}+f_T)P_T(x)+f_{T/d}P^{(\infty)}_{T/d}(x)+f_{\mathrm{BC}}P_{\mathrm{BC}}(x)] \tag{9}$$

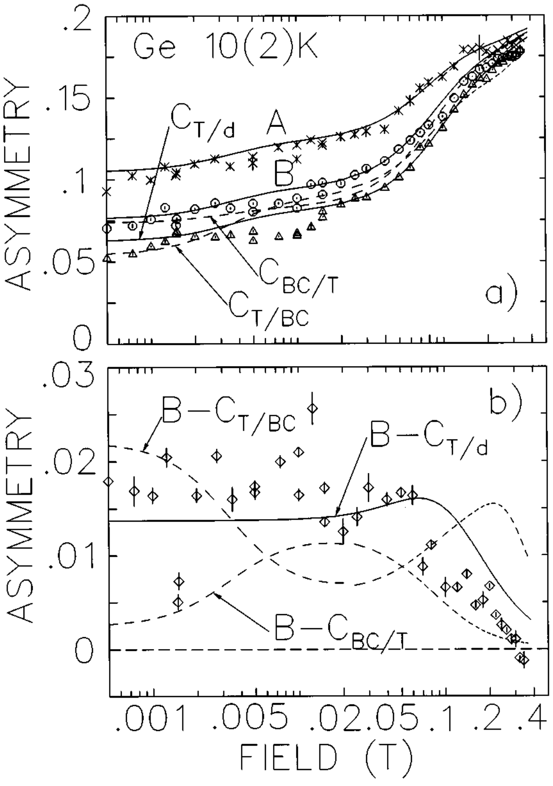

FIG. 3. (a) Longitudinal field dependences of the initial μ-e decay asymmetry (crosses) and the asymptotic ($t\rightarrow\infty$) asymmetry with (circles) and without (triangles) illumination. Solid (A, B, $C_{T/d}$) curves are calculated using the model described in the text. Dashed curves use models including a site change $\mathrm{Mu}_{\mathrm{BC}}{}^0\rightarrow\mathrm{Mu}_T{}^0(\mathrm{C}_{\mathrm{BC}/T})$ or $\mathrm{Mu}_T{}^0\rightarrow\mathrm{Mu}_{\mathrm{BC}}{}^0(\mathrm{C}_{T/\mathrm{BC}})$. (b) The difference in asymptotic asymmetry between illuminated and unilluminated conditions (diamonds), where the curves are calculated from those in (a).

consists of nonrelaxing $\mathrm{Mu}_T{}^0$ and a diamagnetic state slowly generated from $\mathrm{Mu}_T{}^0\rightarrow\mu_d$ conversion. The fractional yield for the former component is about 0.3 ($\equiv f_{+/T}+f_T$), while for the latter it is 0.55 ($\equiv f_{T/d}$). The best fit for dark Ge is obtained when $\nu/\kappa\simeq\frac{1}{3}$ in Eq. (1), with $\nu\sim 10^6\ \mathrm{s}^{-1}$ from the time spectra in Fig. 2. The result is shown as curve B in Fig. 3(a) which reproduces the $A(\infty,x)$ data in dark Ge.

The effect of illumination corresponds to an increase in the ratio ν/κ in Eq. (9) as represented by curve $C_{T/d}$ in Fig. 3(a) [i.e., $A(\infty,x)$ with $\nu/\kappa\simeq 1$]. The residual asymmetry at, e.g., LF$=5\times 10^{-4}$ T [see Fig. 3(a)] then originates solely in the delayed μ_d state [$A_0f_{T/d}/(2+2\nu/\kappa)\simeq 0.03$] and the $\mathrm{Mu}_T{}^0$ state [$A_0(f_{+/T}+f_T)/2\simeq 0.03$], which are not depolarized under illumination. This indicates that the final μ_d state does not interact with excess carriers. The value $\nu/\kappa\simeq 1$ suggests that the conversion process is controlled by the kinetic parameter κ. This is supported by the fact that the effect of illumination is saturated at this photon intensity. Inclusion of a transition process between T and BC sites does not explain the observed change in the repolarization pattern: Figure 3(b) shows that the difference $A_{\nu/\kappa=1/3}(\infty,x)-A_{\nu/\kappa=1}(\infty,x)$ (curve B-$C_{T/d}$) is in reasonable agreement with the data, while other fitting attempts fail to reproduce the gross features of the field dependence.

Earlier experimental results give convincing evidence that the spin relaxation observed in Ge is due to the trapping of muonium by impurity donor atoms (with a concentration of 10^{14} cm^{-3}).[2,12] (Donor impurities lead to higher relaxation rates than acceptors.) The present result is consistent with this model: the observed conversion process is interpreted as

$$\mathrm{Mu}_T{}^0 + d^0 \rightarrow \mathrm{Mu}_T{}^- d^+, \qquad (10)$$

i.e., the trapping of $\mathrm{Mu}_T{}^0$ by a donor atom (Sb) followed by the transfer of an electron from the donor to $\mathrm{Mu}_T{}^0$. (Note that $\nu/\kappa \sim 1$ is also consistent with this interpretation.) Thus the kinetic parameter κ is interpreted as a trapping rate.[2] Another fraction of $\mathrm{Mu}_T{}^0$ is never trapped by donor atoms, and gives rise to the stationary $\mathrm{Mu}_T{}^0$ component in Eq. (9); this is consistent with observations on quantum diffusion of Mu in Na-doped KCl, where a fraction of Mu never encounters the Na impurity.[13] The absence of charge exchange between the final μ_d centers and excess carriers under illumination supports the presumption that the μ_d at this temperature is $\mathrm{Mu}_T{}^-$, and thus different from the diamagnetic component observed at higher temperatures (presumably $\mathrm{Mu}_{\mathrm{BC}}{}^+$). More importantly, this is also in line with the absence of an electronic level associated with $\mathrm{Mu}_T{}^- d^+$ in the band gap, i.e., passivation of the donor level by muonium: an electronic level in the gap can interact with holes and/or electrons near the band gap energy, and so a charged state with its energy level in the gap would be subject to neutralization processes with a rate $\sigma n_p v \sim 10^7$ s^{-1}.

Finally, we note that illumination seems to have no effect either on $\mathrm{Mu}_{\mathrm{BC}}{}^0$ or on isolated $\mathrm{Mu}_T{}^0$. The presence of $\mathrm{Mu}_{\mathrm{BC}}{}^0$ centers is clearly demonstrated by the LF repolarization behavior over the field range below 0.005 T (A in Fig. 3). The residual asymmetry has similar low-field features under both dark and illuminated conditions, indicating that the polarization associated with $\mathrm{Mu}_{\mathrm{BC}}{}^0$ is intact. The analysis in Fig. 3(b) also indicates that the paramagnetic-to-diamagnetic conversion process does not involve $\mathrm{Mu}_{\mathrm{BC}}{}^0$.

Since neither $\mathrm{Mu}_T{}^0$ nor $\mathrm{Mu}_{\mathrm{BC}}{}^0$ seems to interact with photoinduced carriers, it is impossible to tell which is the ground state by the current result. However, the result (together with the fact that $\mathrm{Mu}_T{}^0$ indeed interacts with donors) does indicate that the electronic level(s) associated with muonium in Ge may be as deep as acceptor levels or even not in the energy band gap, in marked contrast with the case in Si where $\mathrm{Mu}_T{}^0$ centers interact with photo-induced carriers efficiently even at 10 K in a fashion quite consistent with the current model in which muonium levels are located in the upper half of the gap[1].

In summary, we have shown that the electronic level associated with the $\mathrm{Mu}_T{}^-$ center in n-type Ge is not located in the energy band gap, as evidenced by its failure to participate in charge-exchange reaction with excess carriers induced by bulk electronic excitation, and in contradistinction to the case of $\mathrm{Mu}_{\mathrm{BC}}{}^+$. The result is consistent with the interpretation that the donor in n-Ge undergoes diffusion-controlled ‘‘muonium passivation.’’ The present study is the precursor of a systematic investigation of the dynamical behavior of these muon states as a function of donor atom concentration and type. Additionally, quantitative information on the nature of the muon-donor interaction will be obtained by observing coupled transitions of the muon and donor using the avoided level crossing resonance technique.[2]

We wish to thank S. Tsuneyuki and Y. Kamiura for helpful discussion, and the RIKEN staff for technical support at RAL. One of the authors (R.M.M.) wishes to acknowledge support from Science and Technology Agency of Japan.

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