

Electric-Field-Enhanced Neutralization of Deep Centers in GaAs

D. G. Eshchenko,^{1,2,*} V. G. Storchak,³ S. P. Cottrell,⁴ and E. Morenzoni²

¹*Physik-Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057, Zürich, Switzerland*

²*Laboratory for Muon Spin Spectroscopy, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*

³*Russian Research Centre “Kurchatov Institute”, Kurchatov Sq. 46, Moscow 123182, Russia*

⁴*ISIS Facility, Rutherford Appleton Laboratory, Oxfordshire OX11 0QX, United Kingdom*

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The charge dynamics of hydrogenlike centers in semi-insulating GaAs have been studied by muon spin resonance in the presence of electric field and RF excitation. Electric-field-enhanced neutralization of deep electron and hole traps by track-induced hot carriers results in an increase of the excess electron's or hole's lifetimes. Similar processes may take place in semiconductor devices working at high voltages and/or under irradiation. As a consequence of the deep traps neutralization, the muonium ($\mu^+ + e^-$) center can capture a hole.

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Since the passivation of shallow acceptors and donors in GaAs by hydrogen was discovered in 1986 [1], the behavior of hydrogen in *III-V* semiconductors has become the subject of intense research. In many respects muonium ($\text{Mu} = \mu^+ + e^-$) can be considered as a light hydrogen isotope ($m_\mu \approx 1/9m_p$). This circumstance stimulated intense studies of semiconductors by muon spin rotation (μSR) techniques (see, for example, [2–6]).

Muon or muonium is studied on a microseconds time scale just after the implantation of high energy (4 MeV) muons and thus is surrounded by its own track products. In a material with long-lived nonequilibrium carriers and large electron mobility, muon can capture a track electron to form muonium. This process of delayed muonium formation formed the basis for the development of the electric field μSR technique (EF- μSR) which can be used as a tool for studying nonequilibrium short range (at distances less than 10^{-4} cm) carrier transport to a positive center in insulators and semiconductors [7,8]. This approach transformed the focus of the μSR experiments from the study of muonium itself to an investigation of the transport properties of semiconducting materials on the microscopic scale. In this Letter we report the further development of μSR technique, in particular, EF- μSR studies using RF excitation (EF-RF- μSR). We demonstrate that using EF-RF- μSR one can look on the recombination processes from the inside of the track, and study fundamental properties of the dominant recombination centers of the host.

As a test material we have chosen semi-insulating (SI) GaAs. SI-GaAs exhibits fascinating optical and electronic properties that have attracted a great deal of attention. Studies of (SI) GaAs are both of fundamental (e.g., the chaos control problem [9]) and of applied (e.g., physics of detectors under irradiation [10]) interest. The semi-insulating properties of GaAs arise from the compensation of residual shallow donors, residual or intentionally added shallow acceptors and intrinsic or intentionally introduced

deep centers. Deep centers are responsible for a lot of metastable physical phenomena including persistent photoconductivity [11] and electrically induced hysteresis effect in the *I-V* characteristics in metal/SI-GaAs/metal structures [12]. Here we demonstrate that EF-RF- μSR can produce an important information on the dynamics of deep centers in GaAs.

The main idea of the radio-frequency μSR experiment in switched electric fields is the following. A relatively large magnetic field is applied parallel to the initial direction of the muon spin (the so-called longitudinal field or LF setup). This maintains a significant muon polarization for both muonium and “diamagnetic” states (bare muon or muon plus two electrons) parallel to the field. To distinguish between the paramagnetic and diamagnetic contributions in the polarization, a small ($H_1 \sim 10$ Oe) RF field is applied perpendicular to the LF at a frequency (~ 20 MHz) tuned to match the Zeeman splitting of the diamagnetic species. Diamagnetic states formed from a paramagnetic (muoniumlike) precursor, even on a microsecond time scale, will contribute to the precessing RF asymmetry with $\omega_{\text{RF}} = 2\pi\gamma_\mu H_1$, where $\gamma_\mu = 0.001355$ kHz/T is the muon gyromagnetic ratio. As most of the track carriers are left behind the stopped muon, we can select the appropriate type of carriers (electrons or holes) to interact with the Muon or muonium by choosing the polarity of the applied electric field (parallel or antiparallel to the muon momentum). A special procedure to fill or neutralize the deep traps in SI-GaAs has allowed us to increase the lifetimes of nonequilibrium carriers and for the first time to study the capture of the holes by Mu. Complementary electric field muon-nuclear level crossing measurements (EF- μLCR experiment) suggest that this process involves muonium at the interstitial tetrahedral position (between four As atoms). This finding prompted us to question the previous understanding about likely donor positions of the interstitial hydrogen in GaAs.

The sample used in these studies is a commercial high resistivity GaAs substrate ($\rho \sim (1.6 - 1.8) \times 10^8 \Omega \text{ cm}$, n -type with an electron mobility $\sim 5000 \text{ cm}^2/\text{Vs}$), 0.5 mm thick, with the (100) crystallographic axis perpendicular to the surface impacted by the muon beam. Silver electrodes of $\sim 80 \text{ nm}$ thickness were deposited on both surfaces of the sample using the DC magnetron sputtering technique, thereby making two Schottky contacts. Most of the experiments reported here were performed at the ISIS pulsed muon facility, located at the Rutherford Appleton Laboratory (RAL, Chilton, UK). The time-differential asymmetry of the muon decay was measured in the standard way as $A(t) = \frac{N_B(t) - N_F(t)}{N_F(t) + N_B(t)}$, where $N_B(t)$ and $N_F(t)$ are decay counts in the backward and forward detectors, respectively [2]. Four sets of histograms are collected: RF-on, positive electric field; RF-on, negative electric field; RF-off, positive electric field; RF-off, negative electric field. The positive electric field points parallel to the initial muon momentum. The states were changed every 1/50 s at every ISIS accelerator frame (i.e., before every muon pulse).

Typical μSR spectra measured in GaAs are presented in Fig. (1). Muonium in GaAs can exist in three charge states Mu^+ , Mu^0 and Mu^- [2,6]. The stable position for Mu^+ lies on the Ga-As bond (so-called Mu_{BC}^+). The tetrahedral void between four As atoms (T_{As}) is also considered [6] as a metastable position supporting Mu^+ . Negative Mu^- is usually placed at the tetrahedral position formed by four Ga atoms or $\text{Mu}_{T_{\text{Ga}}}^-$. Neutral muonium is believed to occupy the bond-center position (Mu_{BC}^0) and both T_{Ga} and T_{As} tetrahedral sites, and is thus denoted by Mu_T^0 . The RF-off asymmetry spectrum consists of a fast-relaxing Mu_T fraction and a slow-relaxing signal which is the sum of the Mu_{BC}^0 and diamagnetic components. The contributions of these two components are resolved in the RF-on spectrum, where the diamagnetic fraction is seen in the precessing

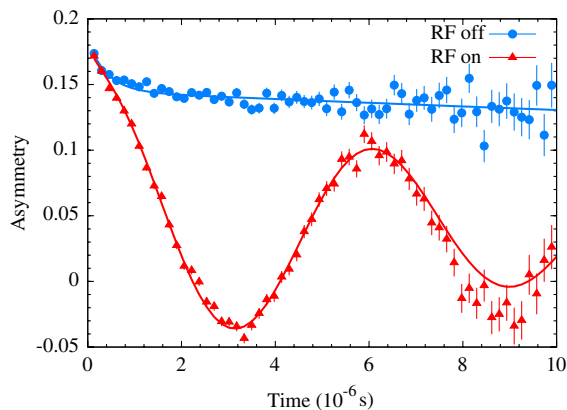


FIG. 1 (color online). Typical experimental spectra (time-differential asymmetry) measured in semi-insulating GaAs after the electric field treatment measured at $T = 70 \text{ K}$ in longitudinal magnetic field $LF = 1837 \text{ Oe}$ and zero electric field. Blue circles: RF signal is off; red triangles: RF signal is on.

signal while the nonrelaxing Mu_{BC}^0 is observed as a constant offset in the spectra. Temperature dependencies of the diamagnetic RF asymmetry (amplitude of the oscillating contribution in Fig. 1) measured in zero electric field are shown in Fig. 2. The triangles represent the temperature dependence of the RF diamagnetic asymmetry in the virgin sample (no electric field history). The increase in the asymmetry (the first complete by 60 K and the second by 120 K) is described in terms of Mu_{BC}^0 to Mu_{BC}^+ conversion [4,6]. Above 120 K the RF asymmetry remains constant and corresponds to $\sim 40\%$ of the apparatus asymmetry in good agreement with the Mu_{BC}^0 fraction measured in transverse magnetic field experiments at low temperatures [2]. This implies that in the virgin sample below 250 K there is no contribution to the diamagnetic fraction from conversion of the Mu_T^0 state, a conclusion in agreement with [6]. The picture changes drastically if, at low temperatures, the sample is treated by applying a large ($E > 10 \text{ kV/cm}$) electric field simultaneously with muon implantation. The enhanced diamagnetic RF asymmetry is shown by the circles. Above $\sim 70 \text{ K}$, the diamagnetic asymmetry in the treated sample exceeds that of the high temperature fraction measured in the virgin sample, implying an additional channel for Mu_T^0 muonium to a diamagnetic state conversion is opened by the sample treatment. Measurements were carried out at a fixed temperature of 70 K to evaluate how the sample changes from its virgin condition to the treated state as a function of exposure to the muon beam. Results are shown by the stars in Fig. (2), each corresponding to a zero electric field measurement carried out after a further 30 minutes of treatment in a field $E = \pm 16 \text{ kV/cm}$. To complete the transition, about two hours of beam exposure or $\sim 1.5\text{--}3.0 \times 10^{15}$ electron-hole pairs

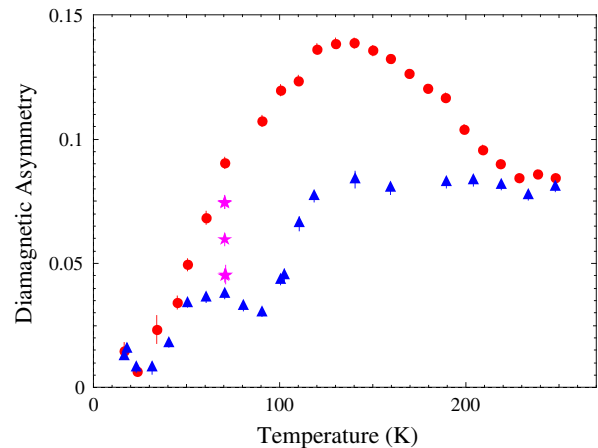


FIG. 2 (color online). Temperature dependencies of the diamagnetic RF asymmetry (amplitude of the oscillating contribution in Fig. 1) measured at zero electric field in different states of commercial SI-GaAs. Triangles: RF diamagnetic asymmetry in the virgin sample. Circles: enhanced RF signal in the treated sample. Stars: RF asymmetry measured in the process of the electric field treatment. All the data were measured on heating.

per cubic centimeter are required. The enhanced RF asymmetry passes through a broad maximum around 120–140 K (a state that persists for at least 12 h), while at temperatures above 140 K it shows annealing behavior and on warming to ~ 220 K the sample is returned to the virgin state.

The origin of the enhanced diamagnetic RF signal can be understood from the electric field measurements. Typical μ SR spectra measured in the treated sample in electric fields ± 1 kV/cm are presented in Fig. (3). Small negative electric fields reduce the precessing RF amplitude to the value measured for the virgin sample, while small positive electric fields have no effect on the amplitude. Taking into account the direction of the effect (positive electric fields point parallel to the incoming muon beam) and recognizing that the injected track carriers are positioned around and mostly behind the stopped muon, the reason for the enhanced diamagnetic signal seems likely to arise from the interaction between the track holes and the Mu_{As}^0 species. A negative electric field will pull holes away from the stopped muon, thereby reducing the muonium to diamagnetic conversion, while a positive electric field will pull out the nearest holes but push “early” track holes towards the stopped muon and muonium to diamagnetic conversion is unchanged. In the virgin sample, a small electric field does not change the RF precessing asymmetry.

To identify the lattice position of the diamagnetic species involved in the enhanced state, muon-nuclear level crossing measurements μ LCR experiments, were performed at the Paul Scherrer Institute, Switzerland. In this technique, integral asymmetry $A(H) = \frac{N_B(H) - N_F(H)}{N_F(H) + N_B(H)}$ (where $N_B(H)$ and $N_F(H)$ are total number of decay counts in the backward and forward detector) is monitored as a function of the applied magnetic field. A resonant transfer of polarization from the muon to the nucleus [or dip in $A(H)$]

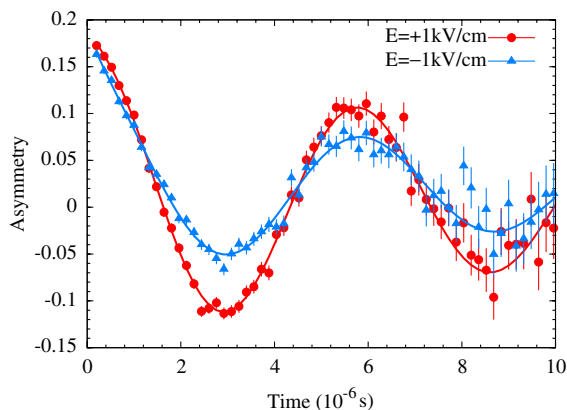


FIG. 3 (color online). Experimental spectra (time-differential asymmetry) measured at $T = 120$ K in SI-GaAs after electric field treatment. Red circles: $E = +1$ kV/cm. Blue triangles: $E = -1$ kV/cm. Small negative electric fields reduce the precessing RF amplitude to the value measured for the virgin sample, while small positive electric fields have no effect on the amplitude.

occurs at a field where the Zeeman splitting for the muon is equal to the combined Zeeman and quadrupole splitting for the neighboring nucleus. For Mu_{BC}^+ the main resonance in our geometry [H parallel to (100)] is expected around $H \sim 1920$ Oe [5]; for Mu_{Ga}^- the resonances are expected at $H < 500$ Oe [3]. We do not see resonances at $H < 500$ Oe. Resonances were, however, detected at a field of ~ 1913 Oe. Results for both small positive and negative electric fields measured in treated SI-GaAs at $T = 120$ K are presented in Fig. 4. The resonance amplitude does not depend on the direction of the electric field, suggesting that the enhanced diamagnetic signal does not belong to the Mu_{BC}^+ state. We therefore need to consider that the tetrahedral As void may be supporting the Mu_{As}^+ state.

The semi-insulating properties of the commercial vertical boat (VB) GaAs substrates are achieved by the compensation of shallow centers by the deep native centers. There are two main models describing the compensation mechanism. A widely accepted theory [13] suggests that the compensation can be attributed to the interaction between the deep intrinsic donors EL2 (an As_{Ga} -related defect which is present at the level $N_{\text{EL2}} \sim 10^{16} \text{ cm}^{-3}$),

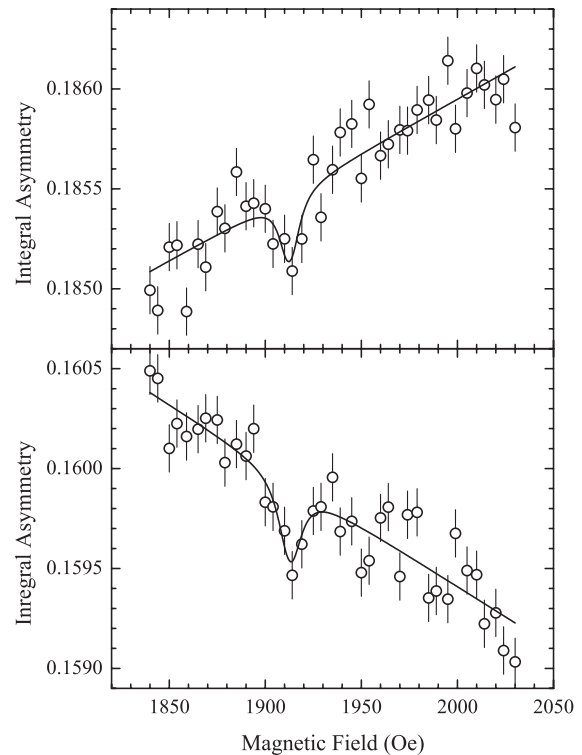


FIG. 4. Muon-nuclear level crossing integral spectra (integral asymmetry vs H) measured at $T = 120$ K in SI-GaAs in the treated state. Top panel: $E = +1.5$ kV/cm. Bottom panel: $E = -1.5$ kV/cm. Electric field is switched with $f = 1$ kHz. The amplitude of the resonance at ~ 1913 Oe does not depend on the direction of a small electric field. Different slopes reflect different Mu_{As}^0 contributions. In negative field Mu_{As}^0 is relaxing; in positive field Mu_{As}^0 is converted to a diamagnetic signal.

residual donors (usually Si) and shallow carbon acceptors which are intentionally introduced in GaAs at the level of $n_C \sim 0.5 \times 10^{15} \text{ cm}^{-3}$. However, thermally stimulated (TS) current in conjunction with TS Hall effect measurements [14] have demonstrated that the concentration of the deep hole traps in SI-GaAs is of the same order as the concentration of the deep electron traps, and that the pinning of the Fermi level on the EL2 midgap may be explained as a result of the balance between deep electron and hole traps. The capture of electrons by the EL2⁺ traps occurs over a configuration barrier with energy of $\sim 0.066 \text{ eV}$ [15]. The applied electric field increases the energy of the carriers and results in enhanced phonon-assisted trapping over the configurational barrier. A similar behavior is observed for the holes traps. Capacitance spectroscopy measurements [16] have revealed that at low temperatures ($T \approx 90 \text{ K}$) a strong electric field ($E \approx 10^4 \text{ V/cm}$) causes an increase of both electron and hole capture cross sections by 5 orders of magnitude for the deep traps in GaAs.

Based on these results we propose the following model for the formation of the enhanced diamagnetic state measured in SI-GaAs. At room temperature, the initial state of the sample is characterized by ionized residual shallow donors, partially ionized EL2 traps and filled by electrons or “ionized” deep acceptor levels (empty holes traps) and ionized shallow acceptor centers. Muon implantation at low temperatures results in the production of nonequilibrium track carriers (electrons and holes) inside the sample. If a large electric field is applied, these carriers are transported through the bulk of the sample and are effectively captured by deep traps. At low temperatures, the thermal emission of electrons or holes from deep traps is negligible, and, consequently, the sample is transferred to a metastablelike state. If the traps are filled, the lifetimes of nonequilibrium carriers are increased and the track electrons or holes can interact with the neutral Mu_7^0 on a microsecond timescale. By considering how small electric fields of opposite polarity affect muonium to diamagnetic state conversion one can conclude that muonium interacts with the its own track holes. As the temperature is increased, electrons and holes are emitted from the filled deep traps, lifetimes for the excess carriers are reduced and there are no holes available for the interaction with muonium regardless of the sign of the applied electric field. The essential part of this model is the presence of both types of deep traps. In contrast, if one follows the simplest model of the SI-GaAs compensation mechanism (where only one deep EL2 electron trap is involved) then the electric field treatment will result to the filling of these traps only and the excess hole lifetime would not increase. An other argument comes from the annealing behavior of our sample. The

well-known metastable state of EL2 recovers in 5 min by being annealed at 130 K [17], while our sample remains in a metastable state for at least 12 h.

In conclusion, we have used the μSR technique in combination with electric fields and RF to probe nonequilibrium carrier dynamics in SI-GaAs and arrived to the following: (i) Below 120 K, the simultaneous bipolar injection and treatment of the sample with high electric fields results in the neutralization of both electron and hole deep traps, and brings the sample to a new metastable state. (ii) As similar conditions (bipolar injection and high electric field) apply for GaAs detectors in high energy physics and x-ray imaging, this finding may have a significant impact on the physics of semiconductor devices, including those working at high voltages and/or under irradiation. (iii) In the SI-GaAs with filled deep traps, excess holes can be captured by muonium put into the tetrahedral cage of four As atoms, where it acts as a filled donor. Similar donorlike behavior is expected for hydrogen. (iv) Our results point to the scenario where not only deep EL2 centers but also deep hole traps are involved in the compensation mechanism in SI-Ga-As.

This work was partially performed at ISIS Pulsed Muon Source, United Kingdom, and at the Swiss Muon Source Facility of the Paul Scherrer Institute, Villigen, Switzerland.

*dimitry.eshchenko@psi.ch

Present address: Institute for Nuclear Research RAS, Moscow 117312, Russia.

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