Shallow acceptor impurities in diamond-like semiconductors studied by polarized negative muons

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Abstract
The results of µSR study of the behavior of shallow acceptor centers in diamond, silicon, and germanium are presented. It was found that the muonic atom, which imitates acceptor in semiconductors, is formed in the paramagnetic state in silicon and germanium at low temperatures whereas in diamond it is formed in the diamagnetic state. The hyperfine interaction constant for the aluminium acceptor center (AC) in silicon was estimated for the first time. It was shown that the main contribution to the relaxation of the magnetic moment of the AC is due to interaction of the AC with the phonon via the Roman process in non-degenerated silicon at temperatures ≤50 K. In the case of germanium, there is an experimental evidence for a change in the contribution of different phonon processes to the relaxation of the AC at temperature ∼10 K. The hole capture rate by the ionized boron acceptor in diamond was determined.

Key words: Muon-spin rotation, semiconductors, acceptor centers, hyperfine interaction

1. Introduction
In spite of the long history of studying impurities in semiconductors, numerous problems still exist in dealing with the basic properties of shallow acceptor centers (AC) in semiconductors with diamond crystal structures (see, e.g. [1]). The hole bound to the acceptor in the ground state in diamond-like semiconductors has the effective angular momentum \( J = \frac{3}{2} \) and is liable to a strong interaction with phonons. As a result, the magnetic moment relaxation rate for the AC in diamond-like semiconductors is very high. The high relaxation rate and the degeneracy of the ground state of the acceptors limit the use of traditional resonance methods for studying these AC.

Capture of a negative muon by a carbon, silicon and germanium atom results in formation of muonic atoms \( \mu B \), \( \mu Al \) and \( \mu Ga \) imitating a boron, aluminum and gallium AC, respectively. The evolution of the polarization of \( \mu^- \) in the 1s-state of a atom is governed by the interaction of the muon spin with the electron shell of the muonic atom (AC) and by interactions of this AC with the media. Therefore, negative muons can be used to study interaction of the AC with the crystal lattice.

As was shown in [2], if the muonic atom is formed in the paramagnetic state (a hole is localized on this atom), there should be relaxation of the muon spin and a paramagnetic shift of its precession frequency:

\[
\frac{\Delta \omega}{\omega} = \frac{\omega_p - \omega_d}{\omega_d} = -\frac{g_{\mu} m_{\mu}}{2 \mu_B^2} \frac{J(J+1) A_{hf} \omega_c}{3 k T},
\]

\[
\lambda = \frac{J(J+1)}{3} \left( \frac{A_{hf}}{\nu} \right)^2 \left( 1 + \frac{\nu^2}{\nu^2 + \omega_c^2} \right),
\]

where \( A_{hf} \) is the hyperfine interaction constant of magnetic moments of the muon and electron shell of the AC; \( \nu \) is the relaxation rate of the AC magnetic moment; \( \mu_B \) and \( \mu_B^* \) are the Bohr magnetons for the electron and the muon; \( h (h = \hbar / 2\pi) \) and \( k \) are the Plank and Boltzmann constants; \( g \) is the g-factor for the AC; \( \omega_p \) and \( \omega_d \) are the muon spin precession frequencies at the paramagnetic and diamagnetic AC; \( \omega_c = g_{\mu_B} B / h \) is the angular frequency of the precession of the magnetic moment of the AC in the magnetic field \( B \); \( T \) is temperature.

The results of the calculations of the probability of the boron, aluminium and gallium AC at equilibrium to be in the paramagnetic state in diamond, silicon and germanium,

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respectively, are presented vs temperature in Fig. 1. The calculations were performed for diamond with the boron concentration \([B]=0.5 \cdot 10^{17} \text{ cm}^{-3}\), for silicon with the aluminum impurity \([\text{Al}]=2 \cdot 10^{13} \text{ cm}^{-3}\) and for germanium with the gallium impurity \([\text{Ga}]=2 \cdot 10^{14} \text{ cm}^{-3}\). The onset of decreasing of the probability slightly moves to higher temperature with increasing of the concentration of acceptor impurity. It is evident that the negative muon may be used to study AC in silicon and germanium at temperatures \(\lesssim 60 \text{ K}\) and \(\lesssim 15 \text{ K}\), respectively.

2. Measurements

The measurements were carried out using the GPD spectrometer [3] located at the \(\mu E1\) muon beam of the Paul Scherrer Institute. The polarization of negative muons was studied in the transverse magnetic field of 0.15–0.25 T in the temperature range of 0.23–300 K.

The time distribution of \(\mu^- \rightarrow e^-\) decay electrons was fitted by the function

\[
N(t) = N_0\left[1 + \frac{P_0}{3} e^{-\lambda t} \cdot \cos(\omega t + \varphi)\right] e^{-t/\tau_{\mu}},
\]

where \(N_0\) is proportional to the number of muons stopped in the sample; \(\tau_{\mu}\) is the life time of the muon in the 1s-state; \(P_0\) is the muon polarization in the 1s-state at \(t = 0\); \(\lambda\) is the muon spin relaxation rate; \(\omega\) and \(\varphi\) are the frequency and the initial phase of the muon spin precession in the magnetic field.

3. Results and discussion

Silicon Twenty Czochralski and one float-zone grown single crystal samples were used for studying the behavior of the AC in silicon, seven boron-doped (\(\lesssim 10^{13}\), 1.3\(\times\)10\(^{15}\), 5.5\(\times\)10\(^{16}\), 1.1\(\times\)10\(^{18}\), 4.1\(\times\)10\(^{18}\), 1.3\(\times\)10\(^{19}\), 4.9\(\times\)10\(^{19}\) cm\(^{-3}\)), two aluminum-doped (2\(\times\)10\(^{14}\), 2.2\(\times\)10\(^{17}\) cm\(^{-3}\)), two gallium-doped (1.1\(\times\)10\(^{15}\), 1.1\(\times\)10\(^{18}\) cm\(^{-3}\)), five phosphorus-doped (3.2\(\times\)10\(^{12}\), 1.6\(\times\)10\(^{13}\), 2.3\(\times\)10\(^{15}\), 4.5\(\times\)10\(^{18}\), 1.2\(\times\)10\(^{19}\) cm\(^{-3}\)), two arsenic-doped (8\(\times\)10\(^{15}\), 2\(\times\)10\(^{17}\) cm\(^{-3}\)), one antimony-doped (2\(\times\)10\(^{18}\) cm\(^{-3}\)), and one germanium-doped (9\(\times\)10\(^{19}\) cm\(^{-3}\))

![Fig. 1. The probability to find the paramagnetic state of the acceptor impurity B, Al, and Ga in diamond, silicon, and germanium, respectively.](image)

![Fig. 2. Paramagnetic shift of the muon spin precession frequency in boron- and phosphorus-doped silicon. The line corresponds to \(\sim 1/T\).](image)

![Fig. 3. The muon spin relaxation rate in boron- and phosphorus-doped silicon. The line corresponds to fit by \(\sim 1/T^\alpha\) (\(\alpha = 2.85 \pm 0.20\)).](image)

(see [4–6]). High-purity phosphorus doped silicon samples with the base size of 9.5\(\times\)9.5 mm\(^2\) and height 22 mm were used to study compression stress effect on the relaxation rate of AC. The samples were oriented so that one of the [111], [110], [100] crystal axes was perpendicular to the prism base plane with the accuracy of \(\pm 1^\circ\).

The temperature dependence of the paramagnetic shift of muon spin precession frequency for the phosphor- and boron-doped samples are presented in Fig. 2. Onset of the deviation from the \(\sim 1/T\) curve corresponds to the beginning of ionization of the paramagnetic \(\mu\)Al. As is seen in n-type silicon, onset of the ionization of the AC does not depend on the impurity concentration. However, for p-type silicon onset of ionization of the AC moves to higher temperature with increasing impurity concentration (IC). This is typical of the n- and p-type samples with IC \(\lesssim 2.2 \cdot 10^{17}\) cm\(^{-3}\) and of the intrinsic sample with germanium concentration \(\sim 9 \cdot 10^{19}\) cm\(^{-3}\). The muon spin precession frequency shift data at temperatures below the onset of ionization of the AC for ten samples were fitted by function (1) and it was found that the mean value of \(A_{nf}\) for \(\mu\)Al in silicon is \(A_{nf}(\mu\)Al)/\(h\) = (26.5\(\pm\)2.3) MHz. This corresponds to the hyperfine field \(B_{hf} = (0.294\pm0.027)\) T at nucleus of AC. Considering the difference of the muon and nucleus magnetic moments, the hyperfine interaction constant for the Al atom in silicon was estimated to be \(A_{hf}(\mu\)Al)/\(h\) = (-2.2\(\pm\)0.2) MHz.

As an example, Fig. 3 shows the temperature depen-
The relaxation rate data were fitted by (2) on the assumption that \( \nu \sim T^\alpha \). It was found that for the n- and p-type samples with the IC \( \lesssim 2.2 \cdot 10^{17} \text{ cm}^{-3} \) the value of the parameter \( \alpha \) is close to 3. The relaxation of the magnetic moment of the AC could be due to its interaction with the phonon (spin-lattice interaction) and spin-exchange scattering of free charge carriers on the AC. The fact that the value of \( \alpha \) does not depend on the IC up to IC\( \lesssim 2.2 \cdot 10^{17} \text{ cm}^{-3} \), and it is the same for silicon with the high concentration of germanium, evidences that relaxation of the AC in these samples is due to interaction with the phonon.

The contribution of free charge carrier scattering to relaxation of the AC was observed at donor or acceptor IC \( > 2.2 \cdot 10^{17} \text{ cm}^{-3} \). For example, \( \nu \) is proportional to \( T^{-1.1} \) (see [5]) at the boron concentration 4.1 \( \cdot 10^{18} \text{ cm}^{-3} \). It is evident that the main contribution to the relaxation of the AC is due to free charge carrier scattering on the AC for samples with IC close to the critical one corresponding to the semiconductor-metal transition (Mott transition).

Theoretical calculations [7,8] predicted power-law dependence of the relaxation rate \( \nu \) of the magnetic moment of the AC in silicon on temperature, and a stronger temperature dependence to be expected for the AC in the uniaxially compressed sample. A considerably increasing lambda in silicon uniaxally stressed by 3 kbar pressure is seen from the data presented in Fig. 4. This corresponds to a decrease in the relaxation of the AC (see equation (2)). It was found that the relaxation rate of the AC is more sensitive to compression of silicon along axis [100]. The decrease in \( \nu \) is due to splitting of the four-fold degenerated ground state of the AC into two Kramers duplets in stressed silicon [9].

**Diamond.** Two CVD diamond film (D2, D5) and three synthetic single-crystal (D1, D3, D4) samples were used to study the behavior of the boron AC in diamond [6,10,11]. Each sample had a total mass of 2 g. The CVD sample was a batch of pieces of several diamond films [12]. The sample D1 was powder of crystallines with sizes 160–180 \( \mu \text{m} \) and samples D3 and D4 were a lot of pieces of a crystal with sizes 2–4 mm [13]. Boron is only dopant which forms AC in diamond. The energy level of boron AC is 370 meV above valence band (see [14]).

The temperature dependence of muon spin polarization \( P_0(T)/P_0(300 \text{ K}) \) and damping rate \( R(T) \) (there \( R \) is used instead of \( \lambda \) in (3), see below) for the sample D5 are presented in Fig. 5. As seen, \( P_0(T)/P_0(300 \text{ K}) \) is constant at \( T > T_0 = 80 \text{ K} \) and drops down to \( \sim 0.45 \) at low temperatures. At the same time, \( R \) is approximately constant at \( T < T_0 \) and shows power-law dependence in the range of 80–220 K.

The values of \( P_0(T) \) at \( T > T_0 \) are close to the maximum possible muon polarization in the ls-state of a carbon atom. Different temperature ranges for different samples where the power-law dependence of the damping rate on temperature were observed. The damping rate data in the range of \( [T_0, T_1] \) were fitted by \( R = C \cdot T^{-\alpha} \). The values of \( T_0, T_1, R_{\text{max}} \), and \( \alpha \) are presented in Table 1.

A pronounced difference of the results for diamond from those for silicon and germanium is that in diamond there was no frequency shift of the muon spin precession within the accuracy of the measurement (\( \Delta \omega/\omega_0 < 5 \cdot 10^{-3} \)). The paramagnetic shift of the muon spin precession frequency in diamond should be larger than that in silicon as the Bohr radius of the acceptor center in diamond is approximately two times smaller than that in silicon (due to the difference in the dielectric constants). The absence of the paramagnetic shift in diamond means that the observed fraction of the muon polarization corresponds to formation of the \( _\mu B \) in the ionized (diamagnetic) state within the time \( \sim 10^{-9} \text{ s} \). The damping – apparent depolarization of the muon – is due to the hole capture by ionized AC and its transition to the paramagnetic state with the rate \( R \). The paramagnetic fraction of the polarization is not visible due to a high precession frequency of the momentum \( F (F = S_\mu + J, S_\mu \) is
the spin of the muon) of the paramagnetic AC in the magnetic field. Very fast decrease of $R$ at $T \sim 220$ K may be due to an increase in the concentration of electrons in the conduction band as a result of release of electrons localized in traps. The effect of the traps in carrier dynamics in CVD diamond was observed in different experiments [15]. To seek for the paramagnetic fraction of the muon polarization in diamond, $Z\!F$ and low magnetic field ($H= 1.0$ mT) at $T=5.2$ K measurements were carried out. The analysis of the experimental data shows that there is no muon spin precession or oscillation signal with a frequency $\Omega < 400$ MHz and an amplitude $> 0.005$. Therefore, "fast" depolarization of the muon in the paramagnetic AC ($\mu$B) has to be assumed.

**Germanium.** The behavior of the polarization of the negative muon in a Ga-doped single-crystal germanium was studied in the transverse magnetic field of 0.25 T. The concentration of gallium was $\sim 3 \cdot 10^{18}$ cm$^{-3}$. The energy level of the Ga acceptor is 11 meV above the valence band [14], its Bohr radius is close to 35 Å [16].

The relaxation and precession frequency shift of muon spin in germanium are observed (see Fig. 6). The relaxation rate of the AC in germanium depends on temperature as $\nu \sim T^{-0.11}$ at $T \leq 10$ K and as $\nu \sim T^{1.8}$ at $T > 10$ K. These results evidences that: 1) the muonic atom $\mu$Ga as the AC forms in the paramagnetic state in a time less $10^{-9}$ s; 2) the ionization probability of the AC increases with temperature at $T > 10$ K, which is in good agreement with the calculation (see Fig. 1).

The temperature dependence of the relaxation rate of the AC at $T \leq 10$ K is unexpectedly very weak and it strongly differs from that above 10 K. Probably, this evidences that the mechanism for the relaxation of the AC magnetic moment changes at $T \sim 10$ K. Three different processes – one-phonon, Raman and Orbach processes – could contribute to the relaxation of the AC (see, e.g. [7]) and the temperature dependence of the relaxation rate is different for these processes. It might happen that in this experiment contributions from the one-phonon and Raman processes are observed as the superseding of one process by the other at about 10 K.

The upper limit for the hyperfine interaction constant of the $\mu$Ga atom was estimated from the frequency shift of the muon-spin precession: $A_{hf} < 10$ MHz. To the best of our knowledge, the $A_{hf}$ for a Ga acceptor in germanium has not been determined until now.

In conclusion, the results for silicon samples presented above are in good agreement with the modern theoretical concept of the shallow AC behavior in semiconductors. For the first time it was experimentally found for the aluminium AC in silicon: a) the hyperfine interaction constant; b) the temperature dependence of the relaxation rate of the AC; c) the AC relaxation mechanism for degenerated (heavy doped) and nondegenerated silicon; d) the dependence of the AC relaxation rate on compression stress on the crystal and on the direction of the stress with respect to the crystal axes.

The hole capture rate $R$ by the ionized boron AC in CVD and synthetic single-crystal diamonds were determined. In diamond the mean time of formation of the muonic atom as the AC in the paramagnetic state is comparable with the muon life time, and $\mu$SR experiments will be used to study charge carrier dynamics.

In germanium very weak temperature dependence of the relaxation rate of the AC was observed at $T < 10$ K and there is evidence for the contribution of different phonon process to the relaxation of AC. Further studies of the germanium samples with different IC would hopefully allow the value of the hyperfine constant to be determined for the AC in germanium and the AC relaxation mechanisms to be clarified.

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**References**


