Near-surface muonium states in germanium

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Abstract

We used the low-energy $\mu$SR technique (LE-$\mu$SR) to extend our previous studies on the energy dependence of muonium (Mu) states in Si and insulators [1] to investigations on an undoped 0.15-mm thick Ge (100) crystal. The Mu formation in the near-surface region from about 10 nm to 150 nm is probed with mean implantation energies between 2.5 and 17.4 keV. In this energy range the number of track electron-hole pairs varies as a function of energy between a few hundred and several thousand [2]. Similar behavior as in Si is observed between 30 K and 150 K, i.e., a doubling of the diamagnetic fraction $F_D$ (Mu$^+$ or Mu$^-$) on lowering the energy $E$ from 17.4 keV to 2.5 keV, corresponding to mean implantation depths of 130 nm and 17 nm, respectively. The fraction of Mu at the tetrahedral interstitial site (Mu$_T$) does not show a pronounced energy dependence. The change of $F_D$ therefore can be attributed to a corresponding change of the bond-center Mu (Mu$_{BC}$) formation probability. This demonstrates that also in Ge the formation of Mu$_{BC}$ clearly depends on the availability of excess charge carriers which the muon creates during the stopping process. Surprisingly, below 50 K $F_D$ starts to increase again for $E > 4$ keV. Additionally, bulk $\mu$SR studies on a piece cut from the same sample shows the opposite trend in $F_D$ below 50 K, and distinct final charge states. More investigations are necessary to clarify this difference.

Key words: muonium formation, semiconductors, low-energy muons

1. Introduction

The final charge state of $\mu^+$ after implantation in insulators or semiconductors can be either positive (Mu$^+$), neutral [Mu$^0 = (\mu^+e^-)$], or negative [Mu$^- = (\mu^+e^-e^-)$]. In semiconductors Mu – which can be considered as a light H isotope ($m_\mu \approx m_p/9$) – is used to identify and investigate the electronic properties and the behavior of isolated hydrogen-like states and impurities [3–5], which are of basic interest due to their influence on the electrical and optical properties of the host material. In Si, Ge and semiconductors of the III-V family two Mu states lying deep in the band gap have been identified at low temperatures ($< 100$ K) [3]: normal Mu$_T$ in the tetrahedral interstitial site with a large isotropic hyperfine interaction (hfI), and anomalous Mu$_{BC}$ at a bond-center between two host atoms with a much smaller, anisotropic hfI. It is now well established that in insulators and semiconductors Mu is formed in two ways: i) during slowing down in charge-exchange collisions where a fraction of muons thermalizes as neutral Mu by elastic collisions, so-called prompt formation, and ii), by capture of an excess electron created in its own ionization track, so-called delayed formation. This has been demonstrated in electric field experiments [6,7] and recently in a study with low-energy muons where the number $N_{ch}$ of excess car-
riers consisting of electron-hole pairs can be directly tuned by changing the $\mu^+$ implantation energy [1]. These experiments have shown that in Si $\text{Mu}_T$ is due to \textit{prompt} formation, whereas $\text{Mu}_{BC}$ is mainly formed by the \textit{delayed} process.

The low-energy $\mu^+ (\text{LE-}\mu^+)$ beam at PSI [8,9] with variable implantation energy $E$ between 1 and 30 keV – corresponding to implantation depths of a few nm up to $\sim 200$ nm – allows the investigation of hydrogen-like $\mu$ impurity states as a function of energy, \textit{i.e.} as a function of $N_{eh}$ and as a function of depth. By varying the energy, $N_{eh}$ can be tuned between a few and several thousand which is up to five orders of magnitude less than for conventional MeV-$\mu$on beams. Below 1 keV nearly no track products are generated.

In this paper, we extend our previous studies on the energy dependence of $\mu$ states in Si and insulators [1] to the first investigation of the energy dependence of the final charge states of $\mu^+$ in undoped Ge (100).

2. Experiment and Results

The sample was a commercial 0.15-mm-thick, 2” single crystal with the $<100>$ direction parallel to the sample normal, polished on both sides, and nominally undoped with a resistivity of $30 \, \Omega \text{cm}$ ($10^{14}$/cm$^3$ charge carrier concentration) at room temperature, supplied by CrysTec, Berlin, Germany. It was glued with conductive silver to a standard sample plate of the LE-$\mu$SR (LEM) setup. A 6-mm-thick sapphire disk between the sample plate and the cold head of the LEM He-flow cryostat ensures good thermal contact at low temperatures and electric insulation; the latter is required to apply up to $\pm 12.5$ kV to the sample for adjustment of the implantation energy of the LE-$\mu^+$. A magnetic field was applied parallel to the $<100>$ direction, which is also parallel to the beam momentum and perpendicular to the muon spin. In a transverse field of 100 G the precession of the muons in diamagnetic environment ($\text{Mu}^+$ in an undoped semiconductor) is observed. A field of 12 G was used to measure simultaneously the precession of the triplet $\text{Mu}_T$ and of the diamagnetic signal. In Ge $\text{Mu}_{BC}$ is usually not observable at these low fields [10]. For the LEM setup at 100 G the $\text{Mu}_{BC}$ precession frequencies $\nu_{34}$ of 59 MHz and 49 MHz are too high to be resolved with the current LEM time resolution, which limits the observable frequency range to about 40 MHz. We tried to observe $\text{Mu}_{BC}$ at a field of 1.7 kG, where in principle $\nu_{34} \approx 35$ MHz is detectable with the LEM setup. However, only about 25% of the $\text{Mu}_{BC}$ amplitude is precessing at $\nu_{34}$; our data at 35 K show an indication for $\text{Mu}_{PC}$ precession at $\nu_{34}$, but statistics were too low in these measurements for a quantitative analysis. Therefore, in the following we focus on the diamagnetic and the $\text{Mu}_T$ signals.

The asymmetries of the diamagnetic precession signal, $A_D$, and the $\text{Mu}_T$ asymmetry $A_{\text{Mu}_T}$ are shown in Fig. 1 as a function of temperature and implantation energy. As an example, the corresponding Gaussian depolarization rates are shown for 17.4 keV and 19.6 keV in Fig. 2. They are as expected for undoped Ge [10,11] and do not depend on implantation energy within the experimental errors.

In Fig. 1 the 17.4-keV data of $A_D$ – corresponding to a mean depth $\langle d \rangle \approx 130 \, \text{nm}$ – are qualitatively similar to bulk measurements [11]: at 260 K the diamagnetic fraction $F_D$ is about 90%, decrease-
ing with decreasing temperature to about 25% at 150 K. This change of the diamagnetic signal is attributed to a corresponding change in the Mu$_T$ and Mu$_{BC}$ signals due to thermally activated ionization and site changing processes of muonium [11]. Below 150 K $A_D$ stays constant and starts to increase again below 50 K. Between 30 K and 150 K a clear energy dependence of $F_D$ is visible. On lowering $E$ to 2.5 keV ($\langle d \rangle \simeq 17$ nm) $F_D$ increases by about a factor two. Since $A_{\text{Mu}_T}$ does not show a pronounced energy dependence – except an outlier at 35 K, see Fig. 1 – this increase in $F_D$ can be attributed to a corresponding decrease of Mu$_{BC}$, which is very similar to the observations in Si [1]. Thus, also in Ge the Mu$_T$ fraction appears to be independent on excess carriers generated by the implanted $\mu^+$ which is consistent with a prompt formation in charge-changing collisions during slowing down. In contrast, the dependence of the Mu$_{BC}$ fraction on the number $N_{eh}$ of excess electron-hole pairs indicates that Mu$_{BC}$ is predominantly formed by the delayed process after the $\mu^+$ stopped at the bond-center between two Ge atoms. The delayed Mu$_{BC}$ formation saturates at $E \sim 17$ keV. This corresponds to a length scale of the the order of 100 nm of the involved muon track, and a required excess carrier number $N_{eh}$ of the order of thousand, consistent with previous results in Si and insulators [1]. Below 100 nm depth the final charge states of near-surface muonium states are significantly changing.

Surprisingly, $F_D$ starts to increase again below 50 K for $E > 4$ keV. We therefore performed additional bulk-$\mu$SR measurements, where the 2”-wafer was cut into $10 \times 10$ mm$^2$ pieces. One of these pieces was studied in the GPS instrument with transverse $\mu^+$ polarization and the field applied parallel to the $<100>$ direction. In front of the sample an Al foil with a thickness of 220 $\mu$m, fixed with a 20-$\mu$m-thick mylar tape, was installed to stop about 75% of the muons in the 150-$\mu$m Ge crystal. The stopping distribution has been calculated with a Monte-Carlo simulation program [12] for a beam momentum of 28 MeV/c, a momentum width of 3% (FWHM), and taking into account additional material (10-$\mu$m-thick mylar and Ti windows, and a 200-$\mu$m beam counter) upstream of the sample. Muons penetrating the Ge sample stopped in Al foil on the rear side of the sample. Thus, about 25% of the diamagnetic signal is background from muons stopping in Al. Measurements were done at 10 G and 100 G to identify Mu$^+$ and Mu$_T$, and at 1.7 kG where the two Mu$_{BC}$ lines $\nu_{34} \sim 35$ MHz and $\nu_{12} \sim 76$ MHz were observable. The asymmetries of the single components as a function of temperature are shown in Fig. 3. The maximum asymmetry in GPS with transverse polarization is 0.21. In Fig. 3 we corrected the asymmetry by taking into account the 25%-fraction of muons stopping in Al. After correction the total asymmetry from the Ge sample is about 0.157.

In contrast to the LEM results the diamagnetic fraction decreases from 30% at 50 K to 10% at 10 K, whereas the 17.4-keV LEM data show an increase from 25% at 50 K to 45% at 10 K. In the LEM data the Mu$_T$ fraction is constant within errors for this temperature range, but it slightly increases in the bulk, as well as the bulk-Mu$_{BC}$ fraction below 20 K. This shows that the decrease of $F_D$ in the bulk is due to an increase of the Mu$_T$ fractions. Also remarkable is the considerable difference of the Mu$_T$ fraction, which is at least two times larger in the bulk measurement. Altogether, below 50 K significant differences develop between the final charge states near the surface ($\sim 100$ nm and less) and the bulk. At 10 K the charge fractions in the bulk are $F_D \sim 10\%,$
$F_{\text{Mu}} \sim 65\%$, and $F_{\text{Mu}_{BC}} \sim 20\%$, with only a small missing fraction. The respective 17.4-keV LEM fractions are $F_D \sim 45\%$, $F_{\text{Mu}_T} \sim 10\%$, and $F_{\text{Mu}_{BC}} \sim 45\%$, if $F_{\text{Mu}_{BC}} = (1 - F_D - F_{\text{Mu}_T})$ is a valid estimate. However, this would mean an unusual large $\text{Mu}_{BC}$ fraction.

![Figure 3](image.png)

Fig. 3. Undoped Ge (100), bulk-$\mu$SR measurement. $A_D$ and $A_{\text{Mu}_{BC}}$ are from 10 G and 100 G TF measurements. The $\text{Mu}_{BC}$ asymmetry $A_{\text{Mu}_{BC}}$, measured at 1.7 kG TF, has been corrected for time resolution and non-precessing amplitude. The maximum asymmetry from the Ge sample after subtracting the Al background is $\sim 0.157$ (dashed line).

The origin of the observed differences between the near-surface muonium states and the bulk states is not clear at the moment. Except orientation and specified resistivity, which indicates undoped material – which is also suggested by the LEM and bulk depolarization rates – details on crystal quality and impurity concentrations are not known. Nevertheless, the data indicate that the present Ge sample is inhomogenous: the crystal quality and/or impurity concentration of the near-surface region up to 150 nm depth could be distinct from the bulk. Different impurity or defect concentrations near the surface could effect the Mu dynamics and therefore the observable final charge states in TF $\mu$SR experiments.

3. Summary

A nominally undoped Ge (100) wafer has been investigated for the first time by LE-$\mu$SR and bulk-$\mu$SR. In LE-$\mu$SR the observed energy dependence of the final charge fractions indicate that $\text{Mu}_{BC}$ is formed by delayed capture of an electron from the ionization track of the muon, whereas $\text{Mu}_T$ forms during slowing down. The final charge state fractions saturate at an implantation energy of about 17 keV, which corresponds to a length scale of the involved muon track of about 100 nm and $N_{\text{ch}} > 1000$ electron-hole pairs. This is quite similar to previous findings in Si [1].

Unexpected observations are i) the increase of the diamagnetic fraction in the near-surface region below 50 K, which is opposite to the bulk, ii) an at least two times smaller $\text{Mu}_T$ fraction in the near-surface region, and iii), very distinct final charges states close to the surface and in the bulk at low temperatures (10 K). More investigations are necessary to clarify these differences.

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References