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The donor nature of muonium in undoped, heavily n-type and p-type InAs

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Abstract
The charge state of muonium has been investigated in p-type doped, nominally undoped (low n-type) and heavily n-type doped InAs. The donor Mu^+ state is shown to be the dominant defect in all cases. Consequently, muonium does not simply counteract the prevailing conductivity in this material. This is consistent with the charge neutrality level lying above the conduction band minimum in InAs.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Hydrogen is a very important, usually electrically active, impurity in semiconductors. It is generally accepted to be a so-called negative-U defect, where the neutral charge state is never thermodynamically stable, with a transition from the positive (donor) charge state to the negative (acceptor) charge state occurring when the Fermi level crosses the so-called H(+/−) transition energy. This energy, which occurs mid-way between the donor [H(+/0)] and acceptor [H(0/−)] levels, normally lies close to the middle of the fundamental band gap, causing hydrogen to counteract the prevailing conductivity of the semiconductor [1]. However, in a number of semiconductors, hydrogen has been predicted [1–6] and in some cases observed [7–11] to act as a donor (acceptor) in already n-type (p-type) material. This occurs, in the former case, when the H(+/−) transition level is located above the conduction band minimum (CBM), and so even for n-type material, the Fermi level can still be below the H(+/−) level leading to hydrogen acting as a donor. Conversely, if the H(+/−) level lies below the valence band maximum, hydrogen can still act as an acceptor, even when the Fermi level lies in the valence band.

The charge neutrality level (CNL) marks the energy at which the charge character of the so-called virtual gap states (ViGS), including surface states, metal- and interface-induced gap states and also defect-induced gap states, changes from predominantly donor-like (when the Fermi level is below the CNL) to acceptor-like (when the Fermi level is above the CNL) [12, 13]. As hydrogen is a very localized impurity centre, it is appropriate to think of this within the ViGS concept; consequently, the location of the H(+/−) level can be equated with the CNL of the semiconductor [1, 11]. In InAs, the CNL is known to be located ∼0.15 eV above the CBM [14, 15], as shown in figure 1. Consequently, this material is also an excellent candidate for hydrogen acting as a shallow donor, even in moderately n-type material. This is in contrast to what is suggested in figure 2 of [1], where the H(+/−) transition level is predicted to occur close to the centre of the band gap.

If a muon is implanted into a semiconductor, it can bind with an electron to form muonium, $Mu = [\mu^+e^-]$, a light isotope analogue of hydrogen. Due to the very well defined decay properties of muons, muon spin rotation (μSR) spectroscopy has been extensively used in order to elucidate spectroscopic information about the behaviour of muonium, and by analogy, hydrogen, in semiconductors [18]. In particular, muonium has been identified as a shallow donor in ZnO [19] and InN [20], supporting the observation of hydrogen as a donor in these materials, and consistent with the CNL lying above the CBM [1, 17], as shown in figure 1. Here, the behaviour of muonium in InAs is investigated by μSR spectroscopy. The donor Mu^+ state is observed to be the dominant centre for both p- and n-type InAs.

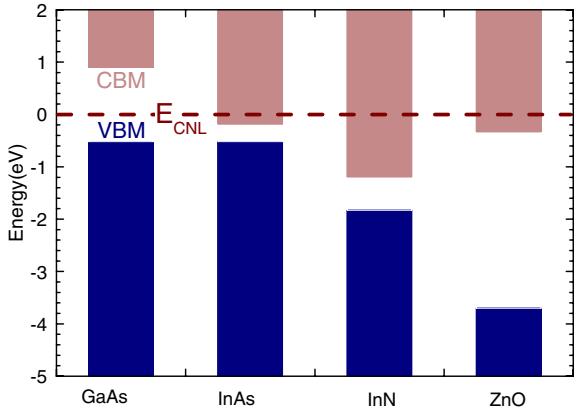

Figure 1. Conduction and valence bands relative to the CNL in GaAs [16], InAs [14], InN [17] and ZnO [1].

2. Experimental details, results and analysis

n-type nominally undoped ($n \approx 2 \times 10^{16}$ cm^{-3} at room temperature (RT)) and S-doped ($n \approx 3 \times 10^{18}$ cm^{-3} at RT) and p-type Zn-doped ($p \approx 2 \times 10^{18}$ cm^{-3} at RT) InAs(001) wafers, from Wafertech, UK, were grown by the Czochralski method, and mechanically polished and chemically etched prior to the μSR experiments being performed. μSR measurements were performed using the EMU end-station at the ISIS Pulsed Muon Facility, Rutherford Appleton Laboratory, UK.

A 100% spin-polarized muon beam was injected into the three differently doped InAs samples in a transverse magnetic field of 10 mT. The samples were mounted in a closed-cycle refrigerator, and measurements performed over the temperature range of 13–300 K. The spin precession is probed via the forward–backward asymmetry of positrons emitted when the muon decays, shown for the undoped InAs sample at 13 and 300 K in figure 2. The oscillatory precession signal is damped due to nuclear dipole interactions. The damping is assumed to be described by a Gaussian envelope and the asymmetry data are fitted by the function

$$A = A_0 \cos(\omega t + \phi) \exp\left(-(\sigma t)^2\right) \qquad (1)$$

where A_0 is the initial asymmetry, ω the Larmor precession frequency, t the time, ϕ a phase, and σ the relaxation rate. A weak (~5% of the main component) non-relaxing component was also required in the fitting to account for a small undamped precession signal from the sample mounting/cryostat windows. The amplitude of this second component as well as the frequency of the main component were fixed for each sample throughout the fitting procedure. The relaxation rate was treated as a free parameter, and the optimum fits for each sample as a function of temperature yielded the relaxation rates shown in figure 3. Fits with all parameters free yield significantly larger uncertainties, but essentially the same $\sigma(T)$ results.

All three samples (nominally undoped, and heavily n- and p-type doped) exhibited very similar relaxation rates as a function of temperature. This is relatively constant at around 0.16 μs^{-1} below 150 K, with a pronounced decrease at around 200 K. A slight increase is then observed above ~250 K.

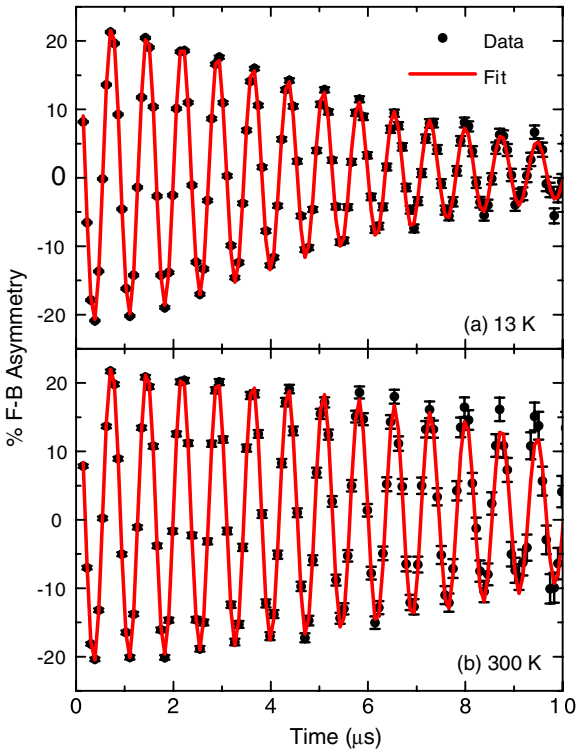

Figure 2. Forward–backward asymmetry and fitting of μSR measurements performed on undoped InAs at (a) 13 K and (b) 300 K in a weak transverse magnetic field (10 mT).

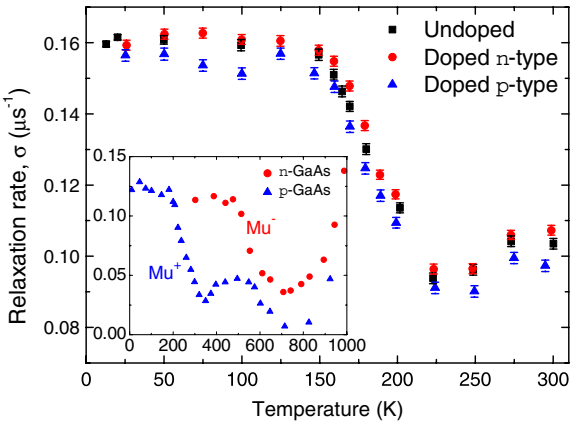

Figure 3. Relaxation rate of the spin precession signal as a function of temperature for undoped, n-type doped and p-type doped InAs. The equivalent plot for GaAs (from [21]) is shown in the inset.

3. Discussion

The decrease in the relaxation rate starting a little below 200 K indicates the onset of diffusion of the muonium. This is consistent with the analysis of zero-field depolarization measurements performed on the same samples, discussed elsewhere [22]. The near equivalence of the relaxation rates in the three samples indicates that the muonium forms in the same charge state in each case. In GaAs, the donor Mu^+ is the dominant charge state for muonium in p-type material, whereas the acceptor Mu^- forms in n-type material,

as expected from the CNL lying close to the middle of the direct band gap, shown in figure 1. The onset of motional narrowing occurs at around 200 K for the donor Mu^+ state in p-type GaAs, whereas the acceptor Mu^- state in n-GaAs is stable up to much higher temperatures (∼500 K), as shown inset in figure 3 [21]. Similar motional behaviour for positively and negatively charged muonium has been observed in a range of zinc-blende III–V semiconductors [23, 24], and would therefore also be expected to be observed here for InAs. By analogy with this, the muonium state in p-type, nominally undoped (low n-type) and heavily n-type InAs can be identified as the donor Mu^+ state. The donor nature of muonium would certainly be expected for the p-type case, further supporting this assignment. Additionally, zero-field depolarization measurements, discussed elsewhere [22], indicate that stationary Mu^+ sits at the bond centre (BC) site, as in GaAs, and that the energy barrier to diffusion via a BC-to-BC path is around 200 meV, similar to the value of ∼220 meV in GaAs [24], compared to a barrier for Mu^- motion of more than 0.6 eV [21].

In an attempt to further confirm the shallow-donor state of muonium in InAs, transverse-field μSR measurements were performed on the nominally undoped InAs sample at temperatures down to 0.3 K. However, using the standard hydrogenic model, the donor binding energy and shallow-donor radius were estimated to be approximately 2 meV and 30 nm respectively. The resulting hyperfine constant proved too small to resolve satellites to the diamagnetic muonium signal, or even to unambiguously identify a change in relaxation rate associated with broadening due to such satellites at temperatures corresponding to energies below the donor binding energy. This is in contrast to, for example, ZnO, where the much larger (smaller) donor binding energy (shallow-donor radius), estimated from the hydrogenic model to be ∼50 meV (1.7 nm), result in a larger hyperfine constant which previously allowed clearly resolved hyperfine-split satellites in the Fourier transform of the asymmetry oscillations to be observed [19].

The existence of the Mu^+ state in n-type InAs indicates that, in this material, muonium does not simply act to counteract the prevailing conductivity. This is consistent with the CNL lying above the CBM, as discussed above, meaning that the H(+/−) transition level, and by extension, the Mu(+/−) level, is located above the CBM. Consequently, it is possible for the Fermi level to be located close to or even above the CBM, leading to significant n-type conductivity, but below the Mu(+/−) transition level, making the donor state still the most favourable.

The most heavily doped sample investigated here has the Fermi level located just above the CNL in InAs. Consequently, hydrogen would be expected to exhibit a slight preference for the formation of acceptors rather than donors. However, from the μSR results presented here, the donor Mu^+ is still the most favourable state for muonium. This suggests that the Mu(+/−) transition level may actually be located somewhat higher in energy than the CNL, and consequently than the H(+/−) transition energy, consistent with previous observations [25, 26].

4. Conclusions

Transverse-field μSR spectroscopy measurements have been performed on n-type nominally undoped, and heavily n- and p-type doped InAs over a temperature range of 13–300 K. Motional narrowing occurs at the same temperature (∼200 K) for all samples, revealing that the donor Mu^+ is the dominant charge state of muonium in all cases. The existence of the Mu^+ state in the nominally undoped n-type sample is consistent with the charge neutrality level being located above the conduction band minimum in InAs. However, Mu^+ still being the dominant charge state for the heavily doped n-type sample, where the Fermi level is located above the charge neutrality level, indicates that the Mu(+/−) transition must occur higher than this, and consequently is expected to lie above the H(+/−) transition.

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