βNMR Study of a Buried Mn δ-doped Layer in a Silicon Host

D Cortie [1,2], T Buck [2], R M L McFadden [3], J Xiao [3], C D P Levy [4], M Dehn [5], M Pearson [4], G D Morris [4], S R Dunsiger [5], R F Kiefl [2], F J Rueß[6], A Fuhrer [6] and W A MacFarlane [1,3]

[1] Quantum Matter Institute, University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada

[2] Department of Physics and Astronomy, University of British Columbia, 6224 Agricultural Road, Vancouver, BC V6T 1Z1, Canada

[3] Chemistry Department, University of British Columbia, Vancouver, BC, V6T 1Z1, Canada

[4] TRIUMF, 4004 Wesbrook Mall, Vancouver, BC V6T 2A3, Canada

[5] Physik-Department, Technische Universität München, James-Franck-Straße 1, 85748 Garching bei München, Germany

[6] IBM Research-Zurich, Säumerstrasse 4, 8803 Rüschlikon, Switzerland

E-mail: `cortie@phas.ubc.ca`

Abstract. Low temperature growth methods were used to encapsulate a buried Mn δ-doping layer into a silicon host. A βNMR investigation was performed of the magnetic properties in the temperature range 10 – 300 K using spin-polarized $^{8}Li^{+}$. A depth-dependent broadening and shift of the NMR resonance was detected that is consistent with internal fields distributed at depths of 10 – 30 nm beneath the surface. At low temperatures, a negative relative shift occurred and the resonance was significantly broadened. At 300 K the line-shape could be described by a single Gaussian line, however, at 10 K the line is best approximated by a two component Lorentzian shape consisting of a broad and narrow component as anticipated for a diluted magnetic alloy. The overall magnitude of the resonance shift at both temperatures is small suggesting a weak interaction between the $^{8}Li^{+}$ and the magnetic Mn environment.

1. Introduction

Precise methods to confine magnetic impurities in silicon are a key step to establishing spin-based functionality in this highly compatible semiconductor. Past work reported high-temperature ferromagnetic behavior in Mn-implanted Si [1], however direct verification of an intrinsic mechanism is complicated by the phase-segregation that occurs during high temperature annealing [2]. By employing low temperature growth methods based on molecular beam epitaxy, it is possible to form buried Mn δ-doped layers embedded in silicon with a tightly confined spatial distribution [3]. We report here on the study of a single buried Mn δ-doped layer encapsulated in silicon. The local magnetic effect of the narrow Mn-distribution was investigated with the sensitive depth-resolved probe of β-detected nuclear magnetic resonance (βNMR) using a beam of radioactive $^{8}Li^{+}$ ions [4, 5]. Based on past βNMR experiments on other magnetic systems, including Mn-doped GaAs [6] and Mn_{12}-molecular monolayers [8], it was predicted that a shifted resonance frequency and a broadened lineshape would provide a sensitive measure of paramagnetic or ferromagnetic behavior in the impurity layer. Here we report on the $^{8}Li^{+}$ NMR resonance at various implant depths and proximities to the δ-doped layer at 10 and 300 K. The results are consistent with a depth dependent magnetic distribution as expected from confined Mn moments in a δ-layer. However, the observed signatures are also substantially different from the ones observed in ferromagnetic Mn-doped GaAs films [6].

2. Experiment

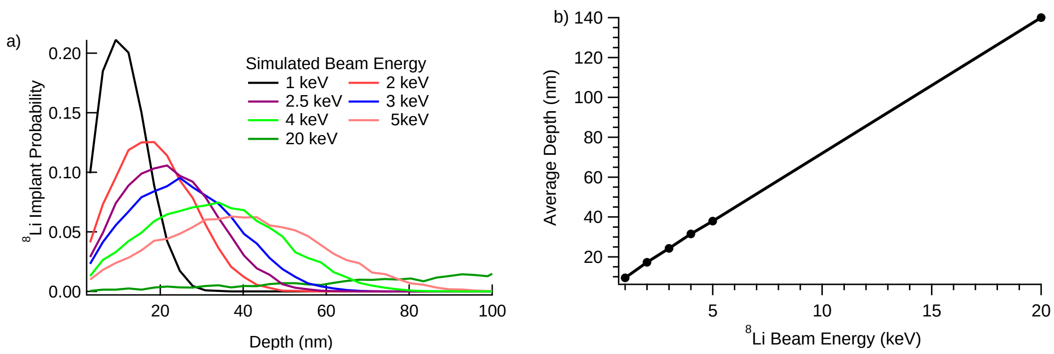

Figure 1. a) Predicted $^8Li^+$stopping range distribution from Monte Carlo simulations at different implant energies and b) Average stopping depth of $^8Li^+$ into Si.

A dual-chamber Omicron VT AFM/STM UHV system was used to deposit surface Mn monolayers and encapsulate these beneath a Si capping layer [3]. The deposition was performed on chemically cleaned p-type B-doped (10Ω cm) Si(100) substrates with carrier densities of approximately 2x10^{15} cm^{-3}. A low concentration of Mn equivalent to 0.2 – 0.3 monolayers was encapsulated at a depth of 10 – 20 nm in a silicon host by using the two step process consisting of low-temperature surface deposition followed by the addition of a Si capping layer. βNMR was used to study the buried magnetic δ-doped region at 10 K and 300 K using ion beams of the nuclear-spin polarized isotope $^8Li^+$ implanted at variable depths in the range 1 – 100 nm. Monte Carlo simulations using the SRIM package were used to predict the penetration depth of the ions into the sample. The experimental study was performed under a high field of 6.55 T applied normal to the substrate surface.

3. Results and Discussion

Figure 1 shows the simulated implantation profile for the $^8Li^+$ calculated using Monte Carlo simulations in the SRIM 2012 software [10]. The addition of a small amount of Mn in the simulated layer profile was found to have negligible effects on the overall distribution which is dominated by the stopping power of silicon, although it should be noted that secondary ion-channeling effects are not modelled by SRIM. It is clear that, for lower ion-beam energies (1 – 5 keV), a substantial portion of Li is expected to stop near the nominal depth of the Mn monolayer (10 – 20 nm). On the other hand, at the highest possible energy (20 keV) there is negligible overlap between the impurity layer and the $^8Li^+$ profile. In general, one would expect the maximum magnetic signal to arise when the probing profile overlaps the magnetic layer. For a magnetic layer buried at 10 – 20 nm, the signal is therefore expected to be maximized at 1 – 3 keV. A common limitation of NMR and βNMR in strongly magnetic materials, however, is the wipeout effect where fast relaxation destroys the observable asymmetry signal. This is a feature of strongly ordered ferromagnetic or antiferromagnetic materials. For this reason it is conceivable that a missing fraction of asymmetry may correspond to $^8Li^+$ located within a few lattice spacings of Mn moments, however as the δ-doped layer is so thin, this fraction will not be large at any energy.

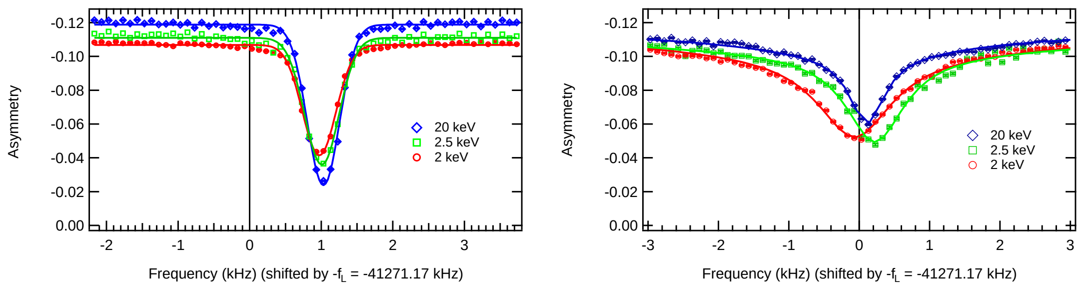

Figure 2. NMR resonance of ^{8}Li$^+$ in Mn-doped Si at a) 300 K and b) 10 K at various probing beam energies. All frequencies have been shifted by the Larmor frequency (f_L) taken from a reference sample. Markers are the data. Solid lines are fits to the data.

Figure 2 a) displays the observed nuclear magnetic resonance at 300 K at various beam energies. The observed resonances are remarkably *narrow*, partly as a result of the absence of nuclear dipolar broadening due to the scarcity of spin-bearing ^{29}Si. In contrast the linewidth is greater than 2 kHz in GaAs due in part to the Ga and As nuclear moments [6]. The narrow line in Si is ideal for measuring small resonance shifts. The resonance shows no quadrupolar splittings indicating that the ^{8}Li$^+$ occupies a site of cubic symmetry, likely the tetrahedral interstitial[7]. It is found that the peak shape can be well described using a single Gaussian. The amplitude of the peak asymmetry for the Mn-doped Si resonance is also quite large even at very low energies of 2 keV. A reduction in amplitude is tied to line broadening from a magnetic origin, but could also result from an increased missing fraction of asymmetry or back-scattering of low energy ions. All of the resonances are a shifted to higher frequencies by approximately 20 parts-per-million (ppm) with respect to the reference frequency, however, it is clear that there are also smaller relative shifts in the resonance frequency corresponding to a depth dependent feature for Li stopping in the range of $10-30$ nm beneath the surface, at some proximity to the Mn layer. The relative shifts between different implantation energies are very small (< 0.1 kHz or ≈ 2 ppm). Past βNMR work on Ga$_{1-x}$Mn$_x$As observed two well-separated resonance peaks corresponding to the magnetic and non-magnetic local environments surrounding the ^{8}Li$^+$ probe [6]. In contrast to that sample, where the magnetic layer was very thick (180 nm), we do not expect a significant fraction of the ^{8}Li$^+$ in the thin δ-doped layer at any energy. Even at the nominally optimal stopping ranges given by $1-2$ keV beam energy (see Fig. 1), less than 20 % of the ^{8}Li$^+$ could be considered to be in the δ-doped layer. Instead, in the neighborhood of the narrow Mn-doped layer, the ^{8}Li$^+$ is expected to sense a distribution of medium-range dipolar fields due to the variable distance between the implant site and the magnetic layer. This would result in an inhomogeneously broadened resonance line. It is clear that the peak width, described by the full-width-at-half-maximum (FWHM) of the Gaussian peaks at 300 K is extremely similar for all beam energies $2-20$ keV (see also Figure 3). We discount the 1 keV data because there is reason to suspect that at these low energies the signal is artificially broadened from a known background signal related to ^{8}Li$^+$ backscattering. The absence of a substantial magnetic effect on the linewidth in this range suggests that any Mn local moment magnetism is highly dynamic and lies in the paramagnetic regime as might be expected at 300 K (e.g. from the behavior of the helimagnet MnSi), or that antiferromagnetic Mn-Mn interactions reduce the net local moment. Past work showed the tendency for Mn to cluster and this cannot be excluded here [3], so that it is possible that nearest-neighbor Mn-Mn interactions play an important role in determining the overall magnetic behavior.

Given the relatively weak magnetic features at room temperature, it is useful to compare the behavior of the same sample at 10 K. If the sample is paramagnetic or ferromagnetic with a

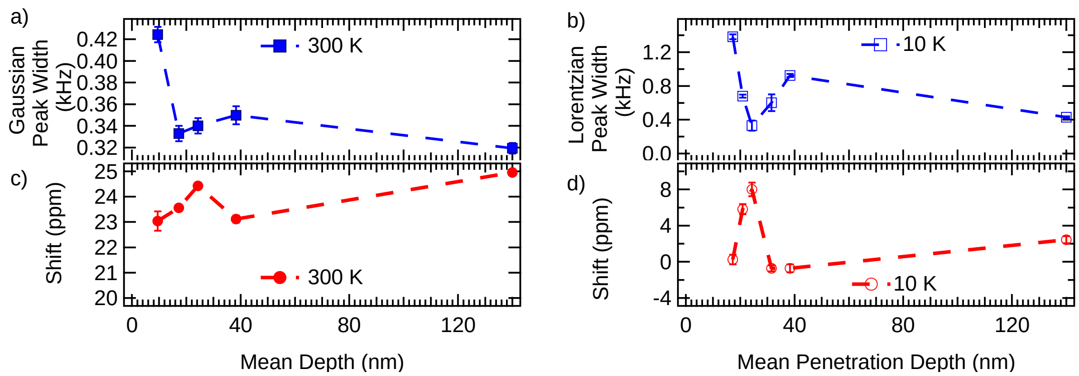

Figure 3. (Top) Summary of the peak-fits of the peak-width at a) 300 K and b) 10 K for various implant depths corresponding to different implant energies. (Bottom) Resonance frequency at 300 K (c) and 10 K (d) for various implant depths.

Curie temperature $\ll$ 300 K, one would anticipate a very strong change in magnetic moment with temperature. The magnetic effects should scale as H/T if the susceptibility is Curie-like. Figure 2 b) shows the observed resonance at 10 K under various different energies with identical RF conditions to those in Figure 2 a). Significant modifications to the line shape and frequency shift are observed at lower temperatures. The resonance overall at low temperature is broadened compared to the room temperature data, and takes on widths approaching 1 kHz. It is found that, unlike the 300 K data, a Gaussian line shape does not accurately describe the 10 K resonance shape, and the best description is a dual-component Lorentzian consisting of a broad and narrow component. A quasi-Lorentzian lineshape is commonly found in NMR studies of dilute magnetic alloys, where a wide range of local magnetic environments reflects the range of distances between the probe nuclei and the dilute magnetic ions [9]. The two Lorenzian components used to fit the 10 K data were found to share a common average frequency and shift within experimental uncertainty. The FWHM of the narrower component was found to be nearly constant ($\approx$ 0.4 kHz) at all beam energies, whereas the wider component varied strongly (0.4 – 3 kHz). The narrow line is ascribed to the intrinsic response of the silicon, whereas the broader component is a feature of the distribution of proximal magnetic fields detected at the $^{8}Li^{+}$ site.

Figures 3 a) and b) summarize the width at various implant depths at room temperature and low temperature respectively. It is clear that the maximum resonance broadening occurs at energies corresponding to depths of 20 – 30 nm suggesting a buried magnetic layer. At 300 K, the FWHM of the peak is nearly independent of the probing depth for energies greater than 1 keV (i.e. for depths greater than 10 nm where backscattering plays little role). However, at lower temperature, the peak-width is strongly depth dependent. Collectively, the room temperature and low temperature data implies that $^{8}Li^{+}$ nuclei located at a depth of $\approx$ 20 nm are sensitive to a magnetic perturbation provided by the Mn impurity which is largely paramagnetic at room temperature and becomes more polarized at lower temperature. The line broadening with different beam energy is quite dramatic at low temperature, and it is likely that the major source is the presence of an inhomogeneous magnetic dipolar field associated with the magnetic layer. It is known, however, that even undoped Si has a slightly broadened resonance at low temperature with a shift that depends on carrier doping [8] and bare GaAs substrates occasionally show a weak depth dependency. Therefore, in order to quantify the magnitude of the Mn-related magnetic field, careful control measurements on our specific doping regime over a range of beam energies are required. Figure 3 c) and d) shows a summary of the fitted frequency at 300 K and 10 K for various penetration depths corresponding to the beam energies 2 – 20 keV. A similar depth-dependent trend is noted in the room temperature and low temperature data. At 300 K and 10 K, the maximum shift and minimum broadening coincide at a penetration depth near 20 nm, corresponding to a beam energy of 2 keV. The relative shifts near the buried feature are far larger at 10 K (+8 ppm) near the magnetic depth profile, than in the room temperature state (+2 ppm) which implies an increased internal magnetic field. It is not yet completely clear whether this distribution is paramagnetic or ferromagnetic in nature, as this will be established using a study of the full temperature dependence. The slight modification of the detection depth between 300 K and 10 K implies the $^8Li^+$ may experience a subtly different magnetic stray field distribution in the room temperature and low temperature state associated with non-random order. Overall, the shift of the resonance deep within the Si substrate is decreased at low temperature, showing that a negative shift relative to the room temperature data is intrinsic to the silicon substrate. This may reflect electron localization resulting in a lower contact hyperfine field at the $^8Li^+$ implant site. The interplay between this effect and magnetic shifts needs to be taken into account and complicates interpretation. The length-scale where the Mn impurity is detected agrees with structural studies on past samples [3], although it is perhaps slightly deeper than the value expected for the deposition times used in the present study (10 − 20 nm). It is possible that the slight difference originates if the SRIM profiles overestimate the implantation depth. Given the relatively high local concentration of the Mn at peak, it is also conceivable that the signal is completely lost for $^8Li^+$ arriving too nearby to the δ layer.

4. Summary

Our initial results show that it is feasible to detect a minute amount of buried magnetic impurity in a silicon host. This is made clear through the systematic beam-energy and temperature dependency of the nuclear magnetic resonance. At room temperature, we observed a single resolved peak that depends on implant energy with maximum shifts appearing at beam energies of 2.5 keV, corresponding to a mean ion range of $\approx$ 20 nm beneath the surface. At lower temperature, the peak was broadened and consisted of a narrow and broad Lorentzian component. This is consistent with a strong temperature dependence in the sample associated with a buried magnetic feature. Future work will aim to investigate Mn-layers buried more deeply into the sample (50 nm) over a wide range of temperatures to track the magnetic transition and ascertain whether it is paramagnetic in nature. In particular, comparison with the blank Si control samples will facilitate quantitative analysis of the internal field distribution.

5. References

[1] M. Bolduc, C. Awo-Affouda, A. Stollenwerk, M. B. Huang, F. G. Ramos, G. Agnello, and V. P. LaBella , Phys. Rev. B **71**, 033302 (2005).

[2] S. Zhou, K. Potzger, G. Zhang, A. Mücklich, F. Eichhorn, N. Schell, R. Grötzschel, B. Schmidt, W. Skorupa, M. Helm, and J. Fassbender , Phys. Rev. B **75**, 085203 (2007).

[3] F.J. Rueß,M. E. Kazzi, L. Czornomaz, P. Mensch, M. Hopstaken, A. Fuhrer, Appl. Phys. Lett. **102**, 082101 (2013).

[4] W.A. MacFarlane et al. , Phys. Rev B **88**, 144424 (2013).

[5] Z. Salman, O. Ofer, M. Radovic, H. Hao, K. H. Chow, M. D. Hossain, C. D. P. Levy, W. A. MacFarlane, G. M. Morris, L. Patthey, M. R. Pearson, H. Saadaoui, T. Schmitt, D. Wang and R. F. Kiefl. , Phys. Rev. Lett. **109**, 257207 (2012).

[6] Q. Song et al., Phys. Rev. B **84**, 054414 (2011).

[7] U. Wahl, Physics Reports **280**, 145 (1997).

[8] Z. Salman, K. H. Chow, R. I. Miller, A. Morello, T. J. Parolin, M. D. Hossain, T. A. Keeler, C. D. P. Levy, W. A. MacFarlane, G. D. Morris and H. Saadaoui, D. Wang, R. Sessoli, G. G. Condorelli and R. F. Kiefl , Nano. Lett. **7**, 1551 (2007).

[9] R. E. Walstedt and L. R. Walker, Phys. Rev. B. **9**, 4857 (1974).

[10] J.P Biersack and L.G. Haggmark, Nucl. Inst. Meth. **174**, 257 (1980).