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Muon States in Polycrystalline and Amorphous Silicon [and Discussion]

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Muon states in polycrystalline and amorphous silicon

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Muons implanted into polycrystalline and amorphous silicon have been studied by transverse-field precession and longitudinal-field repolarization techniques in order to determine the relative fractions and nature of the diamagnetic and paramagnetic trapping sites. A cusp-like dip in the repolarization curves for polycrystalline material is associated with bond-centre muonium and a similar but weaker feature in the amorphous phase is tentatively ascribed to the same species. The relevance of the data to potential sites for hydrogen and its diffusion is discussed.

1. Introduction

The similarities between positive muons and protons in their chemical interactions with atoms can be exploited in muon implantation studies to model the behaviour of hydrogen in semiconductors when detection sensitivity is a problem or where non-equilibrium phenomena occur. In fact our present understanding of the electronic structure of isolated hydrogen defect centres in crystalline silicon derives largely from such studies, including the observation of transient or metastable states favoured by the suddenness of the muon implantation and the microsecond timescale characteristic of μSR spectroscopy.

For muons implanted in crystalline silicon, as well as in various other tetrahedrally coordinated semiconductors, μSR spectroscopy reveals the existence of two paramagnetic states of muonium, i.e. $\mathrm{Mu} = \mu^+e^-$, the pseudo-isotope of hydrogen (see Patterson 1988). As illustrated in figure 1, one of these corresponds to muonium in an interstitial site with tetrahedral symmetry at or near the large cage centres. It is given the notation Mu_T^0, where the superscript denotes the charge state, and is characterized by a muon–electron hyperfine coupling that is isotropic, although with a spin density at the muon only about half that of vacuum-state muonium. Some delocalization of the electronic wave function (although much less than that for substitutional shallow donors) is thereby implied. It appears to be a mobile species, diffusing rapidly between the interstitial cage sites. The other paramagnetic state is immobile, and has a highly anisotropic hyperfine tensor. Commonly denoted Mu*, its identity was uncertain (it is still sometimes referred to as anomalous muonium) until analysis of the tensor, together with chemical arguments, suggested its location at the centre of a Si–Si bond (Cox & Symons 1986), as shown in figure 1. This identification is now substantiated by double-

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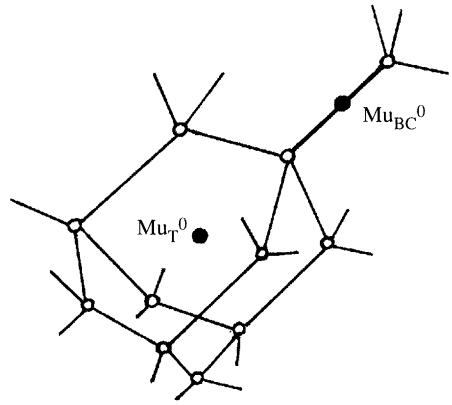

Figure 1. Schematic representation of sites associated with paramagnetic muonium in the silicon lattice. Mu_T^0: interstitial tetrahedral site; Mu_{BC}^0: bond-centre site.

resonance experiments (Kiefl *et al.* 1988) and the corresponding state of hydrogen itself has been detected by ESR spectroscopy (Gorelkinski & Nevinnyi 1991). We therefore denote this bond-centre site as Mu_{BC}^0, the superscript again indicating the charge state. Theoretical modelling confirms the bond-centre site to be the most stable state for an isolated hydrogen (muonium) defect centre and reveals the extent of the relaxation required to accommodate the bond-centre proton or muon (Claxton *et al.* 1993). It seems probable that this local distortion of the lattice represents a barrier to conversion from the metastable Mu_T^0, which carries little or no distortion, to the Mu_{BC}^0 state. This distortion is probably also responsible for the absence of diffusion of Mu_{BC}^0 between neighbouring bond-centre sites.

At low temperatures the above paramagnetic states account for about 95% of muons implanted into crystalline silicon. The remaining diamagnetic fraction may be associated with muonium bound to isolated defects. Figure 2 (solid squares) shows the temperature dependence of the diamagnetic fraction for polycrystalline silicon (pcr-Si) measured by the present authors. Above 150 K, the diamagnetic fraction rises to about 45%, corresponding to ionization of the Mu_{BC}^0 state as evidenced by the loss of its spectroscopic signature (Patterson 1988). At higher temperatures than are displayed in figure 2, the spectroscopic signature of Mu_T^0 also disappears, probably because of conversion to Mu_{BC}^0 and subsequent rapid ionization (see Lichti, this volume), whereafter the diamagnetic fraction rises towards unity.

In the present work, we have sought to examine whether states analogous to Mu_T^0 and Mu_{BC}^0 exist in amorphous silicon and, if so, to what extent their properties are modified. Of particular importance is their possible relevance to the transport states of hydrogen in amorphous silicon. We should, however, bear in mind that, whereas the electron structures of hydrogen and muonium states are expected to be similar, the transport dynamics may differ on account of the larger zero-point energy of the muon relative to hydrogen. (The mass of the muon is approximately one-ninth that of the proton.)

On going from the crystalline to the amorphous host, one could imagine that Mu_T^0 diffusion is suppressed by the loss of periodicity, and that some anisotropy of

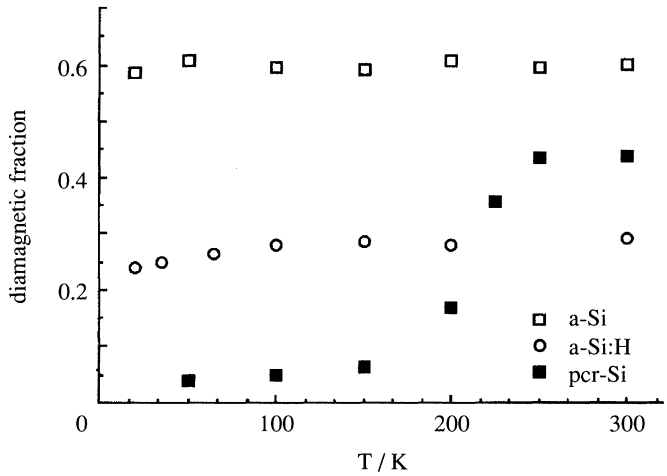

Figure 2. Fraction of muons in a diamagnetic state versus temperature for polycrystalline silicon (pcr-Si), amorphous silicon (a-Si) and amorphous hydrogenated silicon (a-Si:H). The diamagnetic fraction was determined by comparing the amplitude of the muon precession signal in a transverse magnetic field of 20 gauss with that for silver for which the diamagnetic fraction is unity.

the Mu_T^0 hyperfine tensor could develop at asymmetric cage sites. One might also expect that the existence of a degree of strain within the random network could favour the formation of the bond-centre state or catalyse the conversion of Mu_T^0 to Mu_{BC}^0. However, spectroscopic observation of the states is likely to be difficult in a disordered environment. The expected distribution of hyperfine parameters appears to broaden the spectral lines beyond detection and indeed no precession signals resembling either Mu_T^0 or Mu_{BC}^0 are observed by the transverse magnetic field μSR technique in amorphous silicon (a-Si) or in amorphous hydrogenated silicon (a-Si:H) (Davis *et al.* 1991). However, RF resonance techniques reveal a broad spectrum which may be assigned to Mu_T^0-like states (Davis *et al.* 1991).

A further difference in the amorphous state is the existence of a much higher diamagnetic fraction – about 60% for a-Si (open squares in figure 2). This is almost certainly associated with muonium trapped at the numerous dangling bonds present in this material, a conclusion supported by the observation (open circles in figure 2) that this fraction is smaller (*ca.* 25–30%) in hydrogenated samples in which the dangling bond concentration is much suppressed. Another significant difference between pcr-Si and a-Si/a-Si:H revealed in the data of figure 2 is that the diamagnetic fractions of the two amorphous forms are essentially independent of temperature and do not display the step-like rise present in the curve for pcr-Si below room temperature. This suggests a greater stability for Mu_{BC}^0 in the non-crystalline samples.

In the study reported here we have used the longitudinal magnetic field method of muon spin 'repolarization'. In this technique the forward-backward asymmetry in the positron emission which accompanies the muon radioactive decay (2.2 μs) is measured in a direction parallel to the initial polarization vector in the muon beam. This represents the sum of the muon spin projections in each muonium eigenstate, weighted by their occupancies immediately following muon implantation. (We refer here to the incoherent or time-averaged occupancies.) The polarization is in general lower than that of the beam and the manner in which it

varies, as a function of the applied magnetic field, is known as the repolarization or decoupling curve.

2. Theoretical considerations

Repolarization measurements must be made on a timescale that is long compared with the coherent oscillatory evolution and short compared with any spin-lattice relaxation. The first condition is automatically fulfilled in experiments at a pulsed muon source such as ISIS, where the hyperfine oscillations cannot be resolved. The second condition often requires a fitting of the data to a model relaxation function which is then extrapolated back to the moment of muon implantation. This is the case at the higher temperatures in our experiments, where spin-lattice relaxation times approach the microsecond range; at the lower temperatures the relaxation becomes unmeasurably slow.

The repolarization curve for the isotropic $\mathrm{Mu}_{\mathrm{T}}^{0}$ state, with hyperfine interaction $A\boldsymbol{I}\cdot\boldsymbol{S}$, is well known (Brewer *et al.* 1975); it is monotonic and has the analytical form $P(x) = \frac{1}{2} + \frac{1}{2}[x^2/(1+x^2)]$. Here x is the reduced magnetic field, in units of the effective hyperfine field $2\pi A/\gamma_{\mathrm{Mu}}$, where A is the hyperfine constant in frequency units and γ_{Mu} is the gyromagnetic ratio of muonium (essentially that of the electron). The repolarization function arises from equal probabilities that the muon is associated with electron spins parallel and antiparallel to its own spin, the former giving the field-independent fraction $\frac{1}{2}$ and the latter evolving as a high frequency oscillation between eigenstates; only the time average of this oscillatory component is detected and this reflects the decoupling of the hyperfine interaction by the applied field. The repolarization curve for $\mathrm{Mu}_{\mathrm{T}}^{0}$ in silicon is plotted in figure 3 using the known value of the hyperfine constant for this state. When the applied field is comparable to the hyperfine field, the electron and muon become decoupled and the polarization rises towards unity.

For the anisotropic, but axially symmetric, $\mathrm{Mu}_{\mathrm{BC}}^{0}$ state, the hyperfine interaction takes the form $A_{\parallel}I_zS_z + A_{\perp}(I_xS_x + I_yS_y)$, where z defines the axis of symmetry – the $\langle 1\,1\,1\rangle$ directions in crystalline silicon. The repolarization curve for $\mathrm{Mu}_{\mathrm{BC}}^{0}$ depends on the angle θ between this axis and the applied field. Analytical forms are not available for arbitrary orientation and field strength but Patterson (1988) has given curves for θ equal to 0 and 90°. In both cases the polarization, after an initial rise from a value of 1/6th at zero field, exhibits a shallow minimum with magnetic field (Patterson 1988).

As a starting point for modelling the behaviour expected for pcr-Si and a-Si, we have used a calculation of the $\mathrm{Mu}_{\mathrm{BC}}^{0}$ repolarization curve for polycrystalline silicon by Meier (1994) which uses the known hyperfine parameters $A_{\parallel}$ and $A_{\perp}$ and sums the contributions of all possible orientations of the symmetry axis according to a $\sin\theta$ statistical weight. An analytical form for the curve, expressed in terms of the effective hyperfine fields at the muon for the different electron spin states, has been obtained for high fields; this must be combined with a numerical solution at low fields where the electron and muon are not so decoupled. The resulting repolarization curve is found to exhibit a sharp dip, or rather a cusp, at a field determined solely by $A_{\perp}$. This striking feature, shown in figure 3, corresponds to precession of the muon polarization about the perpendicular component of the effective hyperfine field, for orientations where the parallel component can be 'tuned out' with the applied field. Similar features, though with a much smaller

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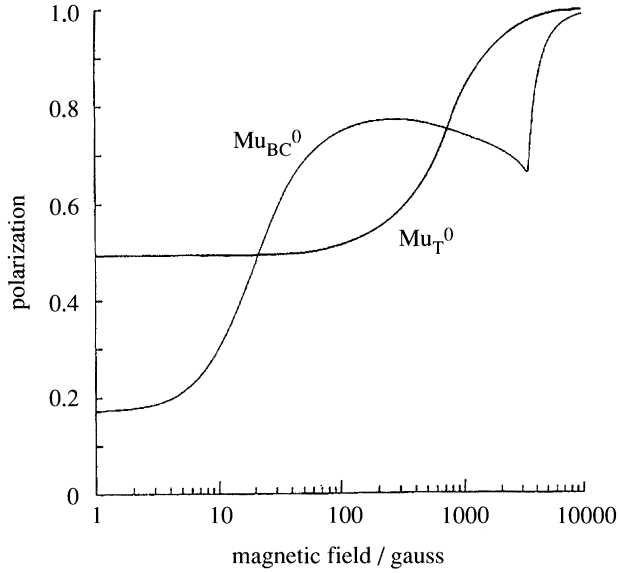

Figure 3. Theoretical repolarization (or decoupling) curves for Mu_T^0 and Mu_{BC}^0 in silicon calculated using the known components of the hyperfine tensors associated with these two species. Note (*a*) the logarithmic scale of magnetic field, (*b*) the low-field values of the polarization (1/2 and 1/6, respectively), (*c*) the earlier rise in polarization for Mu_{BC}^0 compared to Mu_T^0, and (*d*) the cusp at 3400 gauss in the curve for Mu_{BC}^0 (see text).

width relative to the central field, are known for muonium-substituted organic radicals (Roduner 1990).

Such a cusp has been observed in the repolarization behaviour of pcr-Si in experiments undertaken at LAMPF (Cooke *et al.* 1994). This result has been confirmed in runs at ISIS and the dataset extended to include several temperatures. Here we report on these data but, more significantly, demonstrate for the first time the existence of a similar feature in amorphous silicon.

3. Experimental details

A sample of pcr-Si was prepared by grinding a lightly p-doped crystalline wafer to a fine powder with a pestle and mortar. The amorphous sample was obtained by electron-beam evaporation of pieces broken from a slightly p-type single-crystal boule. About 1 g of silicon is needed to ensure that the incident muons are stopped in the sample and about 20 separate deposition runs were required to obtain sufficient material. The deposited films were scraped off the glass substrates and ground to a powder as for the pcr-Si.

The samples were packed into a recess in an aluminium holder, covered with a retaining film of mylar, and mounted in a cryostat. This was positioned in the new EMU muon beamline at the ISIS Pulsed Muon Facility at RAL, inside a magnet capable of producing 4000 gauss in the longitudinal-field configuration required for repolarization measurements. The asymmetry between forward and backward count rates, after suitable instrumental corrections and normalization, was used to determine the polarization as a function of magnetic field strength.

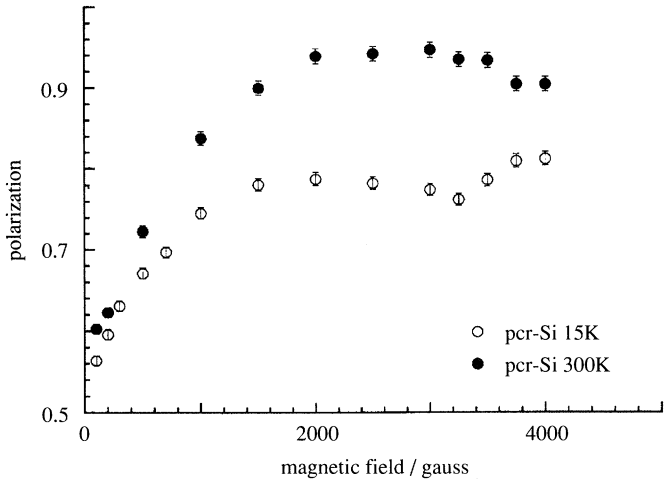

Figure 4. Repolarization curves for pcr-Si at 15 and 300 K. The theoretically predicted cusp is present at the lower temperature but has disappeared at 300 K. (Data not shown here reveals that the cusp is still present, although broadened, at 175 K.) The fall-off at high fields for the 300 K repolarization curve is probably an experimental artefact.

4. Experimental results

Figure 4 displays the repolarization curves for pcr-Si at 15 and 300 K. The cusp, referred to in § 2, is clearly revealed in the 15 K data. Furthermore it occurs at exactly the theoretically predicted field, namely 3400 gauss. It is not present in the curve obtained at 300 K, which is not surprising because this temperature lies above that at which Mu^0_{BC} is known to ionize. Note that the ionization of Mu^0_{BC} results in a higher diamagnetic fraction which serves to raise the overall level of polarization, as observed.

Equivalent curves for a-Si are shown in figure 5. In this case a shallow dip is observed in the curves at both 15 K and 300 K. The feature occurs at a somewhat lower field than in pcr-Si, which suggests either a smaller value of $A_\perp$ for Mu^0_{BC} in the amorphous material or, more likely, a broad distribution of hyperfine constants. Furthermore, in contrast to the situation in pcr-Si, the feature is clearly present at 300 K, implying that Mu^0_{BC} is not so readily ionized in the amorphous phase.

A striking difference between the data displayed in figures 4 and 5 is that the curves at the two temperatures are inverted with respect to each other. That the 300 K curve lies above the one for 15 K for pcr-Si is understandable because, as noted above, the diamagnetic fraction, which is subsumed in the curves, is higher at 300 K in this material and serves to raise the overall level of the curve. In a-Si, the diamagnetic fraction of muonium is almost independent of temperature (see figure 2) and so one might have anticipated that the curves for 15 K and 300 K would lie at a similar level. This apparent anomaly is explained in the next section.

5. Discussion

The observation of the shallow minima in the repolarization curves for a-Si is, we believe, evidence for the existence of a Mu^0_{BC}-like state in this material.

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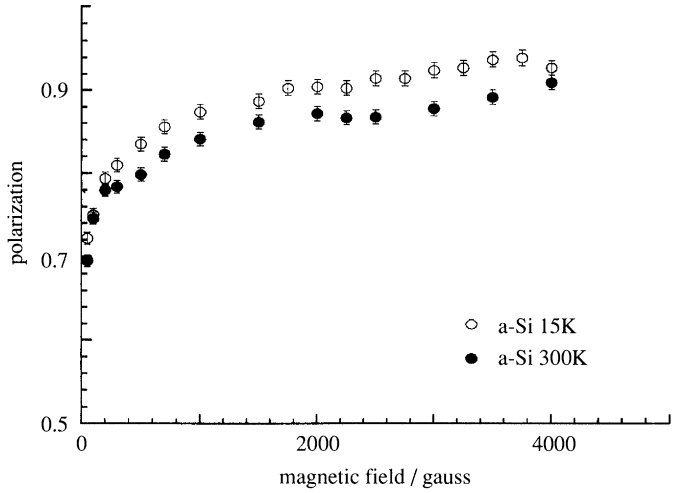

Figure 5. Repolarization curves for a-Si at 15 and 300 K. The remnant of the cusp observed for pcr-Si (see figure 4) is evident in both curves. Its broadening and shift to lower fields compared to pcr-Si can be explained in terms of a distribution in hyperfine constants as might be expected in the amorphous phase. Note the inversion of the two curves relative to those for pcr-Si (see text).

A theoretical set of curves, based on those shown in figure 3, for which the polarization is calculated for a sample containing various ratios of Mu^0_{BC} to Mu^0_T states, indicates that the higher the fraction of Mu^0_{BC}, the lower is the polarization in the region of the cusp (Singh *et al.* 1994). We therefore deduce from the data of figure 5, coupled with the fact that the diamagnetic fraction is independent of temperature, that the Mu^0_{BC} fraction in a-Si is higher at 300 K than at 15 K. This suggests a conversion of Mu^0_T to Mu^0_{BC} as the temperature is raised, which is certainly plausible because Mu^0_{BC} is known to be the more stable species and a higher temperature will aid excitation over the barrier separating the two states. That this conversion is not observed in crystalline silicon is a consequence of the fact that, when conversion does occur, the temperature is already above that at which Mu^0_{BC} ionizes, so the final state is then diamagnetic.

A schematic representation of the binding energies of the various muonium states in both c-Si and a-Si is displayed in figure 6. For c-Si the energies are represented by discrete levels and are positioned, relative to free muonium, on the basis of theoretical calculations (see, for example, Jones 1991; Johnson 1985). The lowest level is not expected to occur in the crystal as it requires an isolated dangling-bond site which does not exist in the crystalline phase except perhaps at dislocations or surfaces. However, it serves as a reference level for the states shown on the right for the amorphous material. These are displayed as broad bands to allow for the variations in site geometries expected in the disordered host.

The lowest energy (highest binding energy) state is that of muonium bonded to a single silicon atom, corresponding to saturation of a dangling bond. This is normally a diamagnetic configuration; just as for passivation by hydrogen, the extra electron is used in forming a covalent bond to the silicon. In n-type material, however, the site might be expected to attract a second electron, in analogy with the so-called D-state in a-Si–H. The two paramagnetic states of muonium, Mu^0_{BC}

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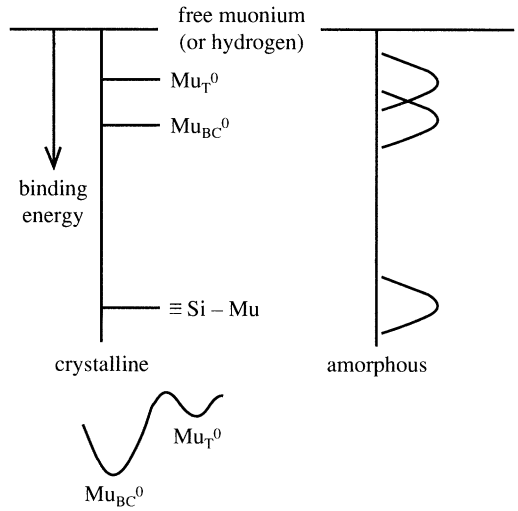

Figure 6. Binding energies of hydrogen (muonium) states relative to the vacuum level for (*a*) crystalline or polycrystalline Si; (*b*) amorphous Si. Also shown is a schematic of the energy barrier between the Mu_{BC}^0 and Mu_T^0 states.

and Mu_T^0, lie at higher energy and we assume here that the bands associated with these are centred at the same energy as the discrete levels in the crystal. The possibility exists, however, that the broadening may be such as to place the lowest levels of Mu_T^0 below the uppermost levels of Mu_{BC}^0.

This energy level scheme is analogous to that proposed by Street for the states of hydrogen in a-Si:H (Street 1991*a*). This material, when prepared by glow-discharge decomposition of silane (SiH_4) – the commonly used method of depositing good electronic-quality films – normally contains between 10 and 20% hydrogen, i.e. far more than is needed to saturate the 0.1% or so of dangling bonds present in unhydrogenated samples. The excess hydrogen occurs predominantly in Si–H_n ($n = 1$, 2 or 3) bonding configurations, apart from a few percent residing in the molecular form (H_2) in interstitial sites (Street 1991*b*). It is conjectured (Street 1991*a*) that a hydrogen atom forming a three-centre bond, analogous to Mu_{BC}^0, is not a stable configuration and that dissociation occurs according to the reaction

$$\equiv\text{Si–H–Si}\equiv \quad \text{——} \quad \equiv\text{Si–H} + \cdot\text{Si}\equiv$$

The resulting unsatisfied dangling bond may then be saturated by a second hydrogen atom during the film growth process. Thus all the hydrogen is eventually incorporated in bonding configurations, analogous to our diamagnetic arrangement, Si–Mu. The existence of sizeable fractions of Mu_{BC}^0 and Mu_T^0 in a-Si, as revealed by the repolarization studies reported here, is not at variance with the generally accepted absence of the corresponding states of hydrogen in a-Si:H. One has to remember that we are observing configurations existing within the timescale of the muon lifetime – not in an equilibrium situation. In fact our results lend support to the model proposed for the diffusion of hydrogen in a-Si:H (Street 1991*a*). In this model, hydrogen, which is mobile above about 200 °C, is excited from the bonded configuration to transport states lying *ca.* 1.5 eV higher in energy. These states are believed to be associated with interstitial sites. The nature of these has not been determined in the case of hydrogen but it seems

likely that they could be associated with the cage and/or bond-centre sites of muonium identified in this study.

6. Conclusions

Longitudinal-field repolarization measurements have verified the existence of bond-centre muonium, Mu^0_{BC}, in pcr-Si by the observation of a theoretically predicted cusp in the decoupling curves. The cusp is present at 15 K but not at 300K, in accordance with conclusions reached from a study of the temperature dependence of the diamagnetic fraction. A similar, but broader, feature has been observed in the curves for a-Si, suggesting that the bond-centre site prevails in the non-crystalline state. The minimum occurs at a lower magnetic field, an observation that is ascribed to a distribution of hyperfine parameters associated with the presence of different local atomic environments.

A study of the temperature dependence of the repolarization curves, coupled with that of the diamagnetic fraction, suggests that the bond-centre site in a-Si is stable to higher temperatures than in pcr-Si. Furthermore the data provide evidence for the conversion of Mu^0_T to Mu^0_{BC}, a process that is unobservable in pcr-Si owing to ionization of the bond-centre site below room temperature.

There seems to be a close similarity between the states of muonium and those of hydrogen in both crystalline and amorphous silicon. It is suggested that the interstitial and bond-centre sites may play a role during diffusion of hydrogen in these materials.

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Discussion

A. M. Stoneham (*Harwell Laboratory, Oxfordshire, U.K.*). One basic question is whether the ionization left behind by the muon affects the system (whether

site or electronic or vibrational state). In a-Si the mobilities are very different from c-Si: is there any effect which is observed associated with this?

E. A. Davis. I presume Professor Stoneham is referring to the mobilities of the electrons or holes. We have not seen any effects that might be attributed to lower carrier mobilities in a-Si but our experiments are probably not sensitive to features in the ionization wake of the muon.

A. M. Stoneham. Does Professor Davis's experience of amorphous silicon give him any idea about what to expect from a-C or a-C:H where there are extra structural features (e.g. graphitic regions)?

E. A. Davis. I would expect muonium to adopt both bond-centre and cage-like sites in the sp^3 bonded regions of a-C, but theory predicts that the Meier cusp for Mu_{BC} should lie at a higher magnetic field than is currently available at ISIS. Neither of the above sites are expected in the sp^2 bonded regions and so one might be able to deduce the relative proportions of sp^3 and sp^2 bonds from the repolarization curves. It would be of interest to study a set of samples prepared under different conditions, with and without H, in order to test these predictions.

M. Symons (*Department of Chemistry and Biological Chemistry, University of Essex, U.K.*). For P centres in silicon, the excess electron is greatly delocalized, but remains associated with a single P^+ unit as established by the ^{31}P doublet hyperfine splitting. In marked contrast, for the comparable centre of N in diamond, the excess electron is in a single N–C s^*-orbital, with major spin density on carbon (Bower, H., and Symons, M.C.R. 1995?). I want to draw an analogy between these two extremes, and the concept on ionization of the bond-centred muonium unit. The latter is quite comparable with the N–C unit. Maybe the ionized form is like the P–Si unit, with the electron delocalized, but still centred on the positive charge. If this is correct, there should be a small residual hyperfine coupling to the muon, but this would be extremely small.