Direct identification of interstitial Mn in heavily p-type doped GaAs and evidence of its high thermal stability

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We report on the lattice location of Mn in heavily p-type doped GaAs by means of β^- emission channeling from the decay of ^{56}Mn . The majority of the Mn atoms substitute for Ga and up to 31% occupy the tetrahedral interstitial site with As nearest neighbors. Contrary to the general belief, we find that interstitial Mn is immobile up to 400°C, with an activation energy for diffusion of 1.7–2.3 eV. Such high thermal stability of interstitial Mn has significant implications on the strategies and prospects for achieving room temperature ferromagnetism in $\text{Ga}_{1-x}\text{Mn}_x\text{As}$.

Intensively studied for over a decade, $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ stands as one of the most well understood dilute magnetic semiconductors (DMS).¹ This sound understanding of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ from both a fundamental and applied point of view, supported by an increase of the Curie temperature (T_C) over the years and by the prominent position of GaAs in semiconductor industry, holds the promise of an eventual crossing of the room temperature barrier and direct technological implementation.

It has been theoretically and experimentally established that the T_C of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ increases with increasing Mn concentration x and hole concentration p .² Thermal annealing near the growth temperature ($\sim 200^\circ\text{C}$) increases p and consequently T_C , but a significant fraction of Mn atoms remains electrically inactive.^{2,3} This partial activation by ($\sim 200^\circ\text{C}$) annealing was attributed to the out-diffusion of a compensating defect with low thermal stability,³ with an activation energy of 0.7 eV,⁴ which has been identified as interstitial Mn.^{4,5}

By studying the lattice location of Mn in heavily p-type doped GaAs, by means of β^- emission channeling, we find evidence of high thermal stability of interstitial Mn.

Emission channeling⁶ makes use of charged particles emitted by a radioactive isotope. The screened Coulomb potential of atomic rows and planes determines the anisotropic scattering of the initially isotropically emitted decay particles. Since these channeling and blocking effects strongly depend on the initial position of the emitted particles, they result in emission patterns that are characteristic of the lattice site(s) occupied by the probe atoms.

A fluence of $2 \times 10^{13} \text{ cm}^{-2}$ of radioactive ^{56}Mn ($t_{1/2} = 2.56 \text{ h}$) was implanted at the ISOLDE facility

at CERN into heavily p-type doped single-crystalline GaAs:Zn ($0.6\text{--}2 \times 10^{-3} \Omega\text{cm}$, $p = 1.4\text{--}6 \times 10^{19} \text{ cm}^{-3}$) with an energy of 50 keV, under a tilt angle of 17° to minimize ion channeling. Using MARLOWE,⁷ the Mn peak concentration is estimated to be $4.6 \times 10^{18} \text{ cm}^{-3}$ at a projected range R_p of 313 Å with a 168 Å straggling. The low Mn concentration allows us to study of the annealing behavior of interstitial Mn (Mn_I) free from phase segregation, which otherwise hinders the quantification of the Mn_I fraction at high annealing temperatures.⁵ On the other hand, the high Zn doping renders the material heavily p-type, similar to typical $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ (DMS) samples. Angular-dependent emission yields of the β^- particles emitted during the decay to stable ^{56}Fe were measured at room temperature, along four crystallographic directions, $\langle 100 \rangle$, $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 211 \rangle$, in the as-implanted state and after *in situ* capless annealing under vacuum ($< 10^{-5} \text{ mbar}$) in steps of 100°C (10 min) up to 600°C . These patterns were recorded using a position- and energy-sensitive detection system similar to that described in Ref. 8. Given the short half-life of ^{56}Mn , this system was installed on-line and upgraded with self-triggering readout chips for the Si pad detectors, enabling measurements during and/or immediately after implantation with count rates of up to several kHz. Quantitative lattice location is provided by fitting the experimental data with theoretical patterns calculated using the *many-beam* formalism for probes occupying different sites with varying root mean square displacement. Calculation and fitting procedures are described in Ref. 6 and Ref. 8, respectively. Details on how the technique discriminates among the possible sites in the GaAs (zincblende) structure are described in Ref. 9.

As a representative example, Fig. 1 compares the normalized experimental β^- emission yields along the four directions [(a)-(d)] measured after 300°C annealing with the best fits of theoretical patterns [(e)-(h)]. These fits correspond to a mixed occupancy of 71% in the substi-

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FIG. 1. (Color online) (a)-(d) Normalized experimental β^- emission channeling patterns in the vicinity of the $\langle 111 \rangle$, $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 211 \rangle$ directions following annealing at 300°C . (e)-(h) Corresponding best fits yielding 71% and 29% of the Mn atoms on S_{Ga} and T_{As} sites respectively.

FIG. 2. (Color online) Comparison between the S_{Ga} (a) and T_{As} (b) simulations and the experimental patterns after 100°C (c), 400°C (d) and 600°C (e) annealing, along the $\langle 211 \rangle$ direction.

tutional Ga site (S_{Ga}) and 29% in the tetrahedral interstitial site with As nearest neighbors (T_{As}). Simple visual inspection (Fig. 2) shows how the features of the $\langle 211 \rangle$ experimental patterns [(c)-(e)] are reproduced by a superposition of the S_{Ga} and T_{As} simulations [(a) and (b)]. It is also clear that this $S_{\text{Ga}} + T_{\text{As}}$ superposition converts into a nearly pure S_{Ga} pattern with increasing annealing temperature. Including S_{As} , T_{Ga} , bond centered (BC), anti-bonding (AB) or hexag-

FIG. 3. (Color online) Fractions of ^{56}Mn on S_{Ga} and T_{As} sites derived from the fits to the experimental patterns: ($\square$) total $S_{\text{Ga}} + T_{\text{As}}$ fraction derived from the $\langle 111 \rangle$, $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 211 \rangle$ best fits; relative fractions on S_{Ga} ($\bullet$) and T_{As} ($\blacktriangledown$) averaged from the $\langle 110 \rangle$ and $\langle 211 \rangle$ best fits; (line) Eq. (1) for $N = 2000$ and $E_a = 1.8$ eV.

onal (H) sites, as well as intermediate positions between pairs of these high-symmetry sites, yields only insignificant fit improvements. Possible fractions on these sites are estimated to be below 5%. The overall results are summarized in Fig. 3. Within the experimental error, the total $S_{\text{Ga}} + T_{\text{As}}$ fraction is 100% for all the annealing steps, confirming negligible occupancy of other sites. Along $\langle 111 \rangle$ and $\langle 100 \rangle$, S_{Ga} and T_{As} are on the same sublattice and therefore the relative fractions on these sites are derived from the fits to the $\langle 110 \rangle$ and $\langle 211 \rangle$ patterns. About 70% of the implanted Mn substitutes for Ga, while the remaining 30% occupies T_{As} sites where it is stable up to 400°C , reducing significantly at 500°C and vanishing at 600°C .

Estimating the activation energy (E_a) associated with Mn_I diffusion requires in principle a detailed knowledge of the concentration profiles of Mn_I and the trapping centers throughout the annealing sequence. However, one can obtain simple estimates for the maximum and minimum E_a values from the following considerations. The total $S_{\text{Ga}} + T_{\text{As}}$ fraction remains constant up to the last annealing stage, indicating that Mn_I converts into Mn_{Ga} by combining with Ga vacancies (V_{Ga}) produced during implantation. Within an Arrhenius model for the thermally activated migration, the fraction $f(T, \Delta t)$ of Mn remaining on T_{Ga} sites after an annealing step of duration Δt at a temperature T is given by

$$f(T, \Delta t) = f_0 \exp[-\nu_0 \Delta t / N \exp(-E_a / k_B T)], \quad (1)$$

where f_0 is the fraction before the annealing step, ν_0 is the attempt frequency, which we take as 10^{12} s^{-1} , i.e. of the order of the lattice vibrations, N is the average number of jumps before a Mn_I atom combines with a Ga vacancy and k_B is the Boltzmann constant.¹⁰ Conservative estimates for the minimum and maximum migration energies can be deduced from the two limiting cases for the value of N corresponding to two opposite scenarios before the mobilization of Mn_I : (1) every Mn_I (in T_{As}) has trapped one mobile V_{Ga} in a neighboring Ga-tetrahedron; (2) Mn_I and V_{Ga} are randomly and independently distributed. The interaction between Mn_I

and other ^{56}Mn or ^{56}Fe atoms can probably be neglected since, not only is the average minimum distance between probes very large (~ 120 Å), the concentration of Ga vacancies is expected to be significantly higher than that of Mn or Fe atoms, i.e., the $\text{Mn}_I\text{-V}_{\text{Ga}}$ interaction dominates.

Case (1) requires a minimum N of one jump of the Mn atom from T_{As} into the Ga vacancy. Case (2) is rather more complex and an accurate solution requires assumptions to be made about the annealing dynamics of V_{Ga} . Nonetheless, one can estimate a maximum value of N from the following. The root-mean-square (rms) distance traveled by a Mn_I atom after N jumps in a 3-dimensional random walk is given by $R_{\text{rms}} = \sqrt{N} \times l$, where l is the distance between two T_{As} sites (4.0 Å). The maximum number of jumps is thus related to the maximum distance traveled by a Mn_I atom before combining with a Ga vacancy, for which a limit can be estimated from our data as follows. Long-range diffusion has a strong effect on the emission patterns due to the exponential dependence of β^- dechanneling on the emitter (^{56}Mn) depth. Diffusion of Mn_I to the surface, i.e. over a distance of R_p , would lead to an apparent increase of fitted fractions. Conversely, diffusion of a similar magnitude into the bulk would damp this fraction, resulting in the opposite effect. Since the total $\text{S}_{\text{Ga}} + \text{T}_{\text{As}}$ fraction remained constant throughout the annealing sequence, one can take R_p as the maximum distance traveled by the Mn_I atoms in the direction perpendicular to the surface. Statistically, only one third of the jumps result in displacements in that direction. The maximum R_{rms} is hence $3 \times R_p$, corresponding to a maximum $N \approx 20000$. Finally, with N between 1 and 20000, Eq. (1) yields an activation energy of 1.7–2.3 eV.

Our results indicate that Mn_I is not the compensating defect that becomes mobile at $\sim 200^\circ\text{C}$ ($E_a = 0.7$ eV) as generally accepted. Interestingly, they do not necessarily disagree with previous element-specific studies on the thermal stability of Mn_I . We note, for example, that although ion channeling measurements qualitatively detected a decrease of the Mn_I fraction after annealing at 282°C ,⁵ they show that at least a significant fraction actually persisted, i.e. almost 100°C above the temperature at which Mn_I would become mobile if it was the low temperature diffuser. Moreover, in a recent radio-tracer study on the diffusion of Mn in GaAs,¹¹ the activation energies for the Mn migration were also found to be very high: ~ 3 eV and higher for the fast and slow components, respectively. However, radio-tracer techniques do not provide direct information on the lattice sites occupied by the diffusing species. In fact, the fast component in Ref. 11 (with $E_a \approx 3$ eV) more likely corresponds to Frank-Turnbull diffusion of the *substitutional* Mn fraction via interstitial sites, since E_a is well above the maximum estimated here for the direct interstitial diffusion of the *interstitial* Mn fraction (2.3 eV).

We should point out that the Mn peak concentration in our experiment was $4.6 \times 10^{18} \text{ cm}^{-3}$ (0.021 %), consider-

ably lower than that of typical $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ DMS materials (few %). While this successfully avoided phase segregation at high annealing temperatures, thus allowing us to study the onset of mobility of interstitial Mn, one must discuss the generalization of our results to $\text{Ga}_{1-x}\text{Mn}_x\text{As}$. According to *ab initio* calculations, the effect of higher Mn concentrations is to increase the activation energy (E_a) for Mn_I diffusion due to the decrease in average $\text{Mn}_I\text{-Mn}_{\text{Ga}}$ minimum distance and the resulting increase in Coulomb attraction between oppositely charged Mn_I (double-donor) and Mn_{Ga} (acceptor) defects.^{4,12} Therefore, if higher Mn concentrations are to have an effect on E_a , that is of increasing it even further away from the 0.7 eV determined for the low temperature diffuser.

Finally, showing that interstitial Mn is immobile in GaAs well above 200°C has significant implications as it motivates a reevaluation of the structural effects of low temperature annealing in $\text{Ga}_{1-x}\text{Mn}_x\text{As}$. This, in turn, may potentially lead to new strategies for achieving pure substitutional doping and higher Curie temperatures.

In summary, we have experimentally established the lattice location of Mn in heavily *p*-type doped GaAs. We confirmed that the majority of the implanted Mn atoms substitute for Ga and located a significant fraction in the tetrahedral interstitial site with As nearest neighbors. Contrary to the general belief that interstitial Mn is mobile at 200°C , we gave evidence of its high thermal stability, up to 400°C , with an effective activation energy for diffusion of 1.7–2.3 eV.

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¹S. Lee, J. H. Chung, X. Liu, J. K. Furdyna, and B. J. Kirby, *Materials Today* **12**, 14 (2009).

²T. Jungwirth, K. Y. Wang, J. Masek, K. W. Edmonds, J. König, J. Sinova, M. Polini, N. A. Goncharuk, A. H. MacDonald, M. Sawicki, A. W. Rushforth, R. P. Campion, L. X. Zhao, C. T. Foxon, and B. L. Gallagher, *Phys. Rev. B* **72**, 165204 (2005).

³T. Hayashi, Y. Hashimoto, S. Katsumoto, and Y. Iye, *Appl. Phys. Lett.* **78**, 1691 (2001).

⁴K. W. Edmonds, P. Boguslawski, K. Y. Wang, R. P. Campion, S. N. Novikov, N. R. S. Farley, B. L. Gallagher, C. T. Foxon, M. Sawicki, T. Dietl, M. B. Nardelli, and J. Bernholc, *Phys. Rev. Lett.* **92**, 037201 (2004).

⁵K. M. Yu, W. Walukiewicz, T. Wojtowicz, I. Kuryliszyn, X. Liu, Y. Sasaki, and J. K. Furdyna, *Phys. Rev. B* **65**, 201303 (2002).

⁶H. Hofass and G. Lindner, *Phys. Rep.* **201**, 121 (1991).

⁷M. T. Robinson, *Phys. Rev. B* **40**, 10717 (1989).

⁸U. Wahl, J. G. Correia, S. Cardoso, J. G. Marques, A. Vantomme, G. Langouche, and ISOLDE Collaboration, *Nucl. Instrum. Methods Phys. Res. B* **136**, 744 (1998).

- ⁹U. Wahl, A. Vantomme, G. Langouche, and ISOLDE collaboration, Nucl. Instrum. Methods Phys. Res. B **148**, 492 (1999).
- ¹⁰U. Wahl, J. G. Correia, E. Rita, J. P. Araujo, J. C. Soares, and ISOLDE Collaboration, Nucl. Instrum. Methods Phys. Res. B **253**, 167 (2006).
- ¹¹O. Koskelo, J. Raisanen, F. Tuomisto, J. Sadowski, and ISOLDE Collaboration, Sem. Sci. Tech. **24**, 045011 (2009).
- ¹²V. I. Baykov, P. A. Korzhavyi, and B. Johansson, Phys. Rev. Lett. **101**, 177204 (2008).