**Effect of the location of Mn sites in ferromagnetic GaMnAs on its Curie temperature**

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ABSTRACT

We report a strong correlation between the location of Mn sites in ferromagnetic Ga$_{1-x}$Mn$_x$As measured by channeling Rutherford backscattering and by particle induced x-ray emission experiments and its Curie temperature. The concentrations of free holes determined by electrochemical capacitance-voltage profiling and of uncompensated Mn$^{++}$ spins determined from SQUID magnetization measurements are found to depend on the concentration of unstable defects involving highly mobile Mn interstitials. This leads to large variations in $T_C$ of Ga$_{1-x}$Mn$_x$As when it is annealed at different temperatures in a narrow temperature range. The fact that annealing under various conditions has failed to produce Curie temperatures above $\sim$110K is attributed to the existence of an upper limit on the free hole concentration in low-temperature-grown Ga$_{1-x}$Mn$_x$As.
In recent years, there is a growing interest in the possibility of using electron spins in electronic devices for the processing, transferring, and storing of information [1]. Many of such applications would require a combination of semiconducting and magnetic properties in the same material. The prospects for the practical realization of such "spintronic" devices increased significantly when it was discovered that alloys of GaAs with Mn (specifically, Ga_{1-x}Mn_xAs with x \approx 0.07) could be made ferromagnetic with a Curie temperature T_C as high as 110 K [2,3].

It was established experimentally that T_C in Ga_{1-x}Mn_xAs increases with increasing Mn concentration x (as long as MnAs precipitates are not formed) and with the hole concentration [3]. These observations are consistent with the Zener model of ferromagnetism proposed by Dietl et al. [4], which predicts

\[ T_C = C p^{1/3}, \]  

(1)

where x is the mole fraction of substitutional Mn^{++} ions, p is the hole concentration, and C is a constant specific to the host material. Alternatively, it has been proposed that the ferromagnetic coupling between Mn^{++} ions is mediated by holes localized on adjacent ions [5].

It should be noted that Mn atoms can occupy three types of sites in the Ga_{1-x}Mn_xAs lattice. Mn atoms can occupy the Ga lattice sites to form the Ga_{1-x}Mn_xAs alloy. They can occupy interstitial sites commensurate with the zinc-blende lattice structure. Finally, Mn atoms can also precipitate out to form different phases (e.g., MnAs inclusions). In the latter case Mn resides at random sites and therefore it is incommensurate with the zinc blende lattice. In Ga_{1-x}Mn_xAs only the substitutional Mn^{++} ions act as acceptors, so that x and p in Eq. (1) are intimately related. As all interstitials of metal atoms Mn interstitials act as donors and tend to passivate substitutional Mn acceptors. Mn atoms which form precipitates (e.g., MnAs inclusions) do not contribute.
free holes, and are thus outside the Zener picture of magnetization. Therefore, to understand the limitations on the maximum $T_C$ in Ga$_{1-x}$Mn$_x$As, it is necessary to address the issue of the lattice site location of Mn, and its relation to the concentrations of both the free holes and of uncompensated Mn$^{2+}$ spins. A few studies addressing the local structures of Mn in III-Mn-V alloys using extended x-ray absorption fine structure (EXAFS) had been reported [6,7]. While accurate determination of near neighbor distances ($<\pm0.005\,\text{Å}$) and local disorders can be achieved using the EXAFS technique, it is not sensitive in measuring the coordination numbers ($\sim20\%$) and distinguishing the chemical nature of the neighbors with small difference in atomic number (e.g. Ga and As). Lattice site location of impurities can only be indirectly inferred from multi-parameter fitting of the EXAFS spectra using calculated model structures.

In this paper we report a study of the lattice sites occupied by Mn atoms in thin Ga$_{1-x}$Mn$_x$As films using channeling Rutherford backscattering (c-RBS) and particle induced x-ray emission (c-PIXE) experiments. The results are combined with measurements (on the same samples) of the free hole concentration, carried out by the electrochemical capacitance-voltage (ECV) profiling; and of magnetization, carried out by SQUID measurements. These studies clearly establish the correlation between the arrangement of Mn sites in Ga$_{1-x}$Mn$_x$As and its Curie temperature.

The Ga$_{1-x}$Mn$_x$As films were grown on semi-insulating (001) GaAs substrate in a Riber 32 R&D molecular beam epitaxy system. Fluxes of Ga and Mn were supplied from standard effusion cells, and As$_2$ flux was produced by a cracker cell. Prior to Ga$_{1-x}$Mn$_x$As deposition we grew a 450 nm GaAs buffer layer at 590°C (i.e., under normal GaAs growth conditions). The substrate was then cooled down to 265°C for the growth of a 3 nm thick low-temperature (LT) GaAs, followed by a 110 nm GaMnAs layer using an As$_2$:Ga beam equivalent pressure ratio of 20:1. Mn concentration in the sample was estimated to be $8 \pm 2\%$ from the change in the growth rate monitored by RHEED oscillations. After the growth, three adjacent $7\times7$ mm pieces of the wafer were cut for
further study. One of these was used as-grown, the other two were annealed at 282°C and 350°C, respectively, for 1 hr in flowing N\textsubscript{2}. The locations of Mn sites in the Ga\textsubscript{1-x}Mn\textsubscript{x}As lattice were then studied by directly comparing the Mn K\textsubscript{α} x-ray signals (c-PIXE) with the c-RBS signals of GaAs from the Ga\textsubscript{1-x}Mn\textsubscript{x}As film simultaneously obtained using a 1.95MeV \textsuperscript{4}He\textsuperscript{+} beam.

The T\textsubscript{C} of the as-grown Ga\textsubscript{1-x}Mn\textsubscript{x}As film was 67K. Annealing at 282°C (i.e. at temperature only slightly higher than the growth temperature) increased the T\textsubscript{C} to 111K. Annealing at 350°C, however, resulted in a lower T\textsubscript{C} of 49K. It has been shown previously that varying the temperature [8] or the duration [9] of the low temperature annealing has produced similar changes of T\textsubscript{C}.

RBS and PIXE measurements on the as-grown Ga\textsubscript{1-x}Mn\textsubscript{x}As sample reveal that the film has a Mn concentration x = 0.09, in good agreement with the value from RHEED oscillations. Figure 1 compares the PIXE spectra from the as-grown Ga\textsubscript{1-x}Mn\textsubscript{x}As film when the crystal is not aligned (random), and when it is aligned in the <110> and <111> directions. The greatly reduced Mn K\textsubscript{α} x-ray yields in the aligned spectra indicates that a dominant fraction of the Mn atoms are shadowed by the lattice site host atoms, and therefore are not visible to the beam along the axial channel direction. The fact that for certain axial channeling projections the Mn atoms are shadowed by the Ga or As atoms indicates that the Mn atoms are in specific (non-random) sites commensurate with the lattice, but does not necessarily imply that the Mn atoms are in substitutional positions. One striking feature shown in Fig. 1 is that the Mn K\textsubscript{α} x-ray yields observed in the <110> alignment are much higher than those in the <111> spectrum. This immediately suggests that the non-random Mn atoms in this sample reside in more than one non-equivalent lattice position.

The normalized yield for the RBS (χ\textsubscript{GaAs}) or the PIXE Mn x-ray signals (χ\textsubscript{Mn}) is defined as the ratio of the channeled yield to the corresponding unaligned yield. The fraction of non-random Mn, f\textsubscript{nr}, can then be calculated by comparing χ\textsubscript{GaAs} and χ\textsubscript{Mn} from
the Ga$_{1-x}$Mn$_x$As film ($f_{nr} = (1 - \chi_{Mn})/(1 - \chi_{GaAs})$) [10]. The $f_{nr}$ in the different channel projections are shown in Fig. 2.

For both the as-grown Ga$_{1-x}$Mn$_x$As film and that annealed at 282°C, the $f_{nr}$ values are similar for the <100> and <111> projections, but show a much lower value for the <110> axial direction. This arises if some Mn atoms are visible in the <110> channel and x-rays coming from these interstitial Mn are enhanced from flux peaking effect in the <110> direction [10,11] and thus $f_{nr}$ calculated from the $\chi_{Mn}$ does not represent the true non-random Mn fraction. For the Ga$_{1-x}$Mn$_x$As film annealed at 350°C, however, the $f_{nr}$ values observed in all directions are similar. Moreover, $f_{nr}$ for all the channeling directions decreases with annealing, suggesting that post-growth annealing promotes random precipitation of Mn. For the specimen annealed at 350°C we estimate that 35% of the Mn atoms form random precipitates. Although it is not possible to identify the form of these random precipitates from the present study, earlier reports on annealing of Ga$_{1-x}$Mn$_x$As or Mn-implanted GaAs suggest that the Mn removed from the ordered sites forms MnAs inclusions when the annealing takes place at temperatures higher than 300°C [12-14].

Figure 3 shows the PIXE and RBS angular scans about the <110> and <111> axes for the three Ga$_{1-x}$Mn$_x$As samples. The angular scans about the <100> directions (not shown) are similar to those about the <111> direction for all three samples. The <110> angular scans are taken along the {110} planar channel. The higher $\chi_{Mn}$ for the as-grown film and for the film annealed at 282°C observed in the <110> direction as compared to those in the <100> and <111> directions suggests that the $f_{nr}$ of Mn atoms in these samples do not all sit in substitutional sites. Specifically, these results indicate that a fraction of these non-random Mn atoms is located at tetrahedral interstitial sites. Atoms in the tetrahedral interstitial positions in a diamond lattice are shadowed by the host atoms when viewed along both the <100> and <111> axial as well as the (100) and (110) planar directions, but are exposed in the <110> axial channel at two equivalent interstitial
positions parallel to the (110) plane and in the (111) planar direction [10,11,15]. This gives rise to a double-peak feature in the <110> angular scan due to the flux peaking effect of the ion beam in the channel. A double-peak feature is indeed observable in the <110> scan for the as-grown sample (indicated by the arrows) shown in Fig. 3. The fraction of these interstitial Mn can be roughly estimated to be ~ 17%, assuming that flux peaking in the <110> channel of GaAs is ~1.5 [10,11,15]. The presence of interstitials in the as-grown film is further confirmed in (110) and (111) planar channeling scans (not shown), where we observed a higher $\chi_{\text{Mn}}$ in the (111) as compared to that in the (110) planar channels. The double-peak feature is less prominent for the sample annealed at 282°C, indicating a reduced concentration of interstitial Mn in this sample. This suggests that the Mn interstitials are unstable, and precipitate out as Mn clusters and/or MnAs upon annealing. The fact that $\chi_{\text{Mn}}$ in the sample annealed at 350°C are high and nearly equal in all the three channeling scans further suggests that not only all of the interstitial Mn, but also a significant fraction of the Mn atoms originally at the substitutional (cation) sites, leave their positions to form random precipitates.

It is well known that the determination of the hole concentration in ferromagnets is complicated by the so-called anomalous Hall effect (AHE), characteristic of conducting ferromagnets [3,16]. To circumvent this problem, we have used the electrochemical capacitance voltage (ECV) profiling method to measure the depth distribution of uncompensated Mn acceptors in the $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ layers [17]. This method provides information on the distribution of the net space charge in the depletion region. The ECV profiling showed an increase of the net acceptor concentration from $6 \times 10^{20} \text{cm}^{-3}$ observed in the as-grown sample to $1 \times 10^{21} \text{cm}^{-3}$ for the $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ film annealed at 282°C [18]. The sample annealed at 350°C, on the other hand, showed practically no change in the hole concentration. We have verified the validity of the ECV method by comparing ECV and Hall measurements on (non-magnetic) heavily Be-doped LT-GaAs. The ECV results are consistently within 10% of the Hall values of free hole concentration.
We can therefore assume that there are no donor levels close to the valence band and the ECV measurements reflect the free hole concentration in the Ga$_{1-x}$Mn$_x$As films. The ion channeling and ECV results show that out of $\sim 2 \times 10^{21}$ cm$^{-3}$ Mn atoms in the as-grown Ga$_{0.91}$Mn$_{0.09}$As only $6 \times 10^{20}$ cm$^{-3}$ can act as electrically active uncompensated acceptors. A small fraction ($\sim 10\%$) of the remaining atoms form random (or possibly coherent) Mn and/or MnAs clusters. Arsenic antisite (As$_{Ga}$) donors can also compensate some of the substitutional Mn acceptors. Most important, however, the PIXE results show that in the as-grown sample a significant fraction ($\sim 17\%$) of the Mn atoms reside on interstitial sites. The interstitial Mn (designated Mn$_I$) are highly mobile positively charged donors. They can, however, be immobilized by occupying the interstitial sites adjacent to the negatively charged substitutional Mn$_{Ga}$ acceptors, thus forming Mn$_I$-Mn$_{Ga}$ pairs, and rendering Mn$_{Ga}$ inactive as acceptors.

Annealing the sample at 282°C (only slightly above the growth temperature) breaks the relatively weak Mn$_I$-Mn$_{Ga}$ pairs, releasing the highly mobile Mn$_I$ to diffuse to available substitutional sites or to form precipitates and/or clusters, thus leaving behind the substitutional Mn$_{Ga}$, which can then become electrically-active acceptors. Consequently the 282°C annealing leads to a higher hole concentration, $p = 1 \times 10^{21}$ cm$^{-3}$ and a higher concentration of Mn atoms occupying random sites. The very high hole concentration, about an order of magnitude higher than the concentration limits in p-type GaAs [20,21] indicates that the sample annealed at 282°C is still far from thermodynamic equilibrium. This is confirmed by the annealing at 350°C that drives the system towards equilibrium by removing the Mn from the electrically active Mn$_{Ga}$ sites, to form random precipitates and/or clusters. Such mechanism has already been shown to be a driving force that limits the free hole concentration in heavily Zn doped GaAs [21]. It should be noted here that, contrary to earlier suggestions, [9] the arsenic antisite (As$_{Ga}$) defects are not expected to play a significant role in the annealing-induced changes, since these latter defects have been shown to remain stable up to 450°C [22].
Measurements of magnetization very nicely corroborate these results. The saturation magnetization $M_s$ observed at 5K on a number of Ga$_{1-x}$Mn$_x$As specimens annealed at 282°C increases by approximately a factor of 1.5 relative to the values of $M_s$ measured on the same specimens before annealing. This clearly supports the conclusion that the low temperature annealing breaks antiferromagnetically ordered Mn$_I$-Mn$_{Ga}$ pairs leading to higher concentration of uncompensated Mn spins. Note that, according to the ECV results, annealing increased the hole concentration $p$ from ca. 6x10$^{20}$ cm$^{-3}$ to 1x10$^{21}$ cm$^{-3}$, by a ratio of about 1.7, in reasonable agreement with the increase in the uncompensated magnetic moments, as indicated by the behavior of $M_s$. Also we find that the annealing-induced increase of $T_C$ from 67 K to 111 K scales very well with the corresponding increase in the free hole concentration. This result further confirms the assertion that the total number of the ferromagnetically coupled spins is related to the concentration of uncompensated Mn ion acceptors rather than the total number of Mn atoms.

Our results show that the large changes in the electronic and magnetic properties induced by the annealing at temperatures so close to the growth temperature can be attributed to the lattice site rearrangement of highly unstable Mn$_I$. The fact that our maximum $T_C$ of 111 K is so close to the maximum $T_C$ of 110 K reported by other groups [2,3,9] suggests the possibility that this could be a fundamental limit on $T_C$ in Ga$_{1-x}$Mn$_x$As alloy system. If so, this may be the reason why similar maximum values of $T_C$ were found in Ga$_{1-x}$Mn$_x$As with rather different values of $x$, ranging from 0.053 to 0.091 [3,9].

It is well known that the formation energies and thus also the concentrations of charged defects such as Mn$_I$ donors or Mn$_{Ga}$ acceptors are to a large extent controlled by the Fermi energy [20]. To maximize $T_C$ one strives to increase the concentration of electrically active Mn$_{Ga}$ acceptors, and thus also the concentration of uncompensated Mn spins. This, however, leads to a downward shift of the Fermi energy, that in turn
increases the formation energy of negatively charged defects, thus making the incorporation of new Mn_{Ga} acceptors energetically unfavorable. It is therefore reasonable to expect that there is a hole concentration limit, beyond which additional Mn can only be incorporated in the form of Mn_{I} donors and/or electrically inactive precipitates. Our results indicate that in the low-temperature-grown materials the maximum T_{C} is achieved for the hole concentration limit \( p_{\text{max}} = 10^{21} \text{ cm}^{-3} \), which requires Ga_{1-x}Mn_{x}As with \( x > 0.045 \). While this value is quite large, we note that a similar hole concentration limit (\( p = 8 \times 10^{20} \text{ cm}^{-3} \)) has been also found in a nonmagnetic Be doped, low temperature grown GaAs [19,23]. It should be emphasized that any detailed description of the microscopic mechanism limiting the maximum Curie temperature will have to consider the role of As antisites donors [24,25].

In conclusion, we have shown that the location of Mn sites in the Ga_{1-x}Mn_{x}As lattice plays a crucial role in determining its magnetic properties. The concentrations of free holes and of uncompensated Mn spins, both of which underlie the ferromagnetic properties in the III_{1-x}Mn_{x}V alloys, are thus seen to be controlled by the behavior of unstable defects involving highly mobile Mn interstitials. In particular, the Curie temperature of Ga_{1-x}Mn_{x}As is clearly affected by the rearrangement of the Mn atoms in the crystal lattice. The relationship of T_{C} to the behavior of Mn interstitials thus leads to wide variations of this parameter for annealing even in a narrow temperature window. Finally, we note that the observed limit for maximum Curie temperature can be attributed to the limit on the free hole concentration attainable in low temperature grown Ga_{1-x}Mn_{x}As.

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FIGURE CAPTIONS

Fig. 1  PIXE spectra from the as-grown Ga$_{1-x}$Mn$_x$As film when the crystal is not aligned (random) and aligned in the $<110>$ and $<111>$ directions.

Fig. 2  The non-random fractions of Mn for the three different Ga$_{1-x}$Mn$_x$As films as calculated from the values of $\chi_{\text{GaAs}}$ and $\chi_{\text{Mn}}$ in the different channel projections.

Fig. 3  Angular scans about the $<110>$ and $<111>$ axes for the three Ga$_{1-x}$Mn$_x$As samples. The $<110>$ angular scans are taken along the \{110\} planar channel.
Fig. 1
Fig. 2
Fig. 3

Normalized yield, $\chi$

- <110> scan
  - Host (RBS)
  - Mn (PIXE)
  - As-grown

- <111> scan
  - Host (RBS)
  - Mn (PIXE)
  - As-grown

Temperatures:
- 282°C
- 350°C

Tilt angles (degree):
- $-2.0$ to $2.0$