

Effect of the location of Mn sites in ferromagnetic $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ on its Curie temperature

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We report a strong correlation between the location of Mn sites in ferromagnetic $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ measured by combined 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^{2+} spins determined from superconducting quantum-interference device 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 $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ 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 ~ 110 K is attributed to the existence of an upper limit on the free hole concentration in low-temperature-grown $\text{Ga}_{1-x}\text{Mn}_x\text{As}$.

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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, $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ 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 $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ 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 that

$$T_C = Cxp^{1/3}, \quad (1)$$

where x is the mole fraction of substitutional Mn^{2+} 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^{2+} 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 $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ lattice. Mn atoms can occupy the Ga lattice sites to form the $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ 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 $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ only the substitutional Mn^{2+} 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 that 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 $\text{Ga}_{1-x}\text{Mn}_x\text{As}$, 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 ($< \pm 0.005$ Å) and local disorders can be achieved using the EXAFS technique, it is not sensitive in measuring the coordination numbers ($\sim 20\%$) 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 multiparameter 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 $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ 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 superconducting quantum-interference device (SQUID) measurements. These studies clearly establish the correlation between the arrangement of Mn sites in $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ and its Curie temperature.

The $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ 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 $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ 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 $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ layer using an As_2 :Ga beam equivalent pressure ratio of 20:1. The Mn concentration in the sample was estimated to be $(8 \pm 2)\%$ from the change in the growth rate monitored

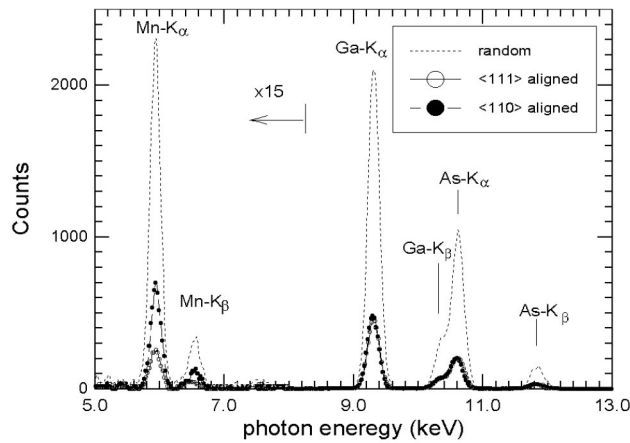


FIG. 1. PIXE spectra from the as-grown $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ film when the crystal is not aligned (random) and aligned in the $\langle 110 \rangle$ and $\langle 111 \rangle$ directions.

by reflection high-energy diffraction (RHEED) oscillations. After the growth, three adjacent $7 \times 7 \text{ mm}^2$ pieces of the wafer were cut for further study. One of these was used as-grown, the other two were annealed at 282 and 350 °C, respectively, for 1 h in flowing N_2 . The locations of Mn sites in the $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ lattice were then studied by directly comparing the Mn $K\alpha$ x-ray signals (c-PIXE) with the c-RBS signals of GaAs from the $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ film simultaneously obtained using a 1.95-MeV $^4\text{He}^+$ beam.

The T_C of the as-grown $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ film was 67 K. Annealing at 282 °C (i.e., at temperature only slightly higher than the growth temperature) increased the T_C to 111 K. Annealing at 350 °C, however, resulted in a lower T_C of 49 K. It has been shown previously that varying the temperature⁸ or the duration⁹ of the low-temperature annealing has produced similar changes of T_C .

RBS and PIXE measurements on the as-grown $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ 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 $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ film when the crystal is not aligned (random), and when it is aligned in the $\langle 110 \rangle$ and $\langle 111 \rangle$ directions. The greatly reduced Mn $K\alpha$ x-ray yields in the aligned spectra indicate 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 (nonrandom) 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 $K\alpha$ x-ray yields observed in the $\langle 110 \rangle$ alignment are much higher than those in the $\langle 111 \rangle$ spectrum. This immediately suggests that the nonrandom Mn atoms in this sample reside in more than one *nonequivalent* lattice position.

The normalized yield for the RBS (χ_{GaAs}) or the PIXE Mn x-ray signals (χ_{Mn}) is defined as the ratio of the channeled yield to the corresponding unaligned yield. The fraction of nonrandom Mn, f_{nr} , can then be calculated by com-

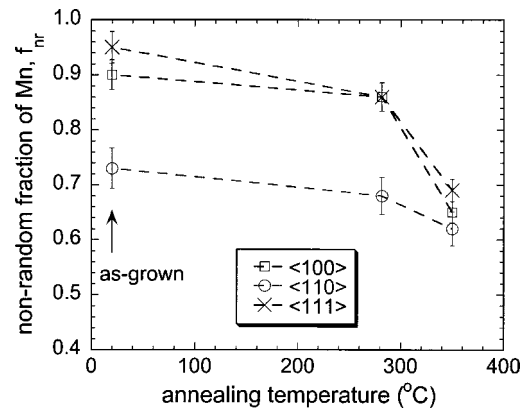


FIG. 2. The nonrandom fractions of Mn for the three different $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ films as calculated from the values of χ_{GaAs} and χ_{Mn} in the different channel projections.

paring χ_{GaAs} and χ_{Mn} from the $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ film [$f_{\text{nr}} = (1 - \chi_{\text{Mn}})/(1 - \chi_{\text{GaAs}})$].¹⁰ The f_{nr} in the different channel projections are shown in Fig. 2.

For both the as-grown $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ film and that annealed at 282 °C, the f_{nr} values are similar for the $\langle 100 \rangle$ and $\langle 111 \rangle$ projections but show a much lower value for the $\langle 110 \rangle$ axial direction. This arises if some Mn atoms are visible in the $\langle 110 \rangle$ channel and x rays coming from these interstitial Mn are enhanced from the flux peaking effect in the $\langle 110 \rangle$ direction,^{10,11} and thus f_{nr} calculated from the χ_{Mn} does not represent the true nonrandom Mn fraction. For the $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ 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 $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ 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 $\langle 110 \rangle$ and $\langle 111 \rangle$ axes for the three $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ samples. The angular scans about the $\langle 100 \rangle$ directions (not shown) are similar to those about the $\langle 111 \rangle$ directions for all three samples. The $\langle 110 \rangle$ angular scans are taken along the $\{110\}$ planar channel. The higher χ_{Mn} for the as-grown film and for the film annealed at 282 °C observed in the $\langle 110 \rangle$ direction as compared to those in the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions suggest 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 nonrandom 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 $\langle 100 \rangle$ and $\langle 111 \rangle$ axial as well as the $\langle 100 \rangle$ and $\langle 110 \rangle$ planar directions, but are exposed in the $\langle 110 \rangle$ axial channel at two equivalent interstitial positions parallel to the $\langle 110 \rangle$ plane and in the $\langle 111 \rangle$ planar direction.^{10,11,15} This gives rise to a double-peak feature in

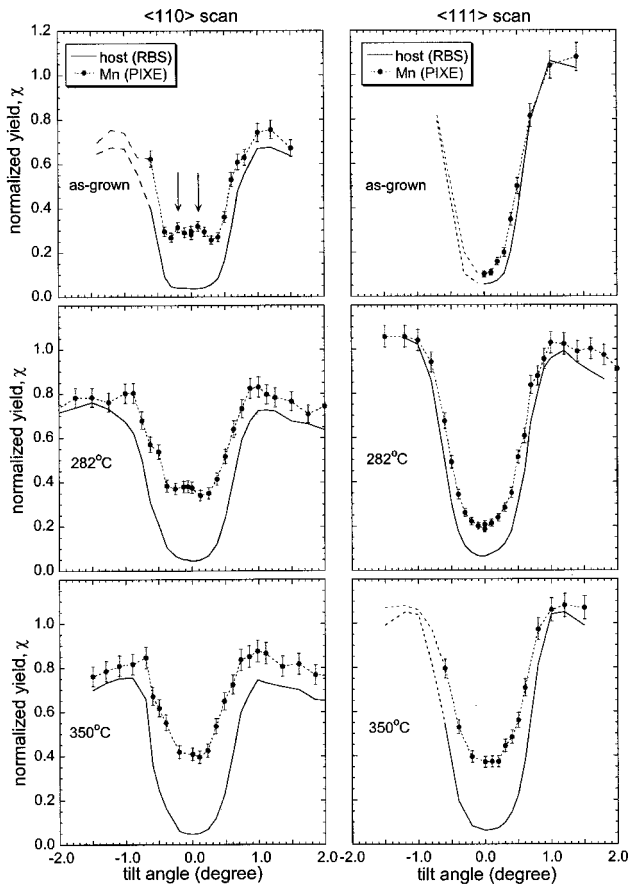


FIG. 3. Angular scans about the $\langle 110 \rangle$ and $\langle 111 \rangle$ axes for the three $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ samples. The $\langle 110 \rangle$ angular scans are taken along the $\{110\}$ planar channel.

the $\langle 110 \rangle$ angular scan due to the flux peaking effect of the ion beam in the channel. A double-peak feature is indeed observable in the $\langle 110 \rangle$ scan for the as-grown sample (indicated by the arrows) shown in Fig. 3. The fraction of these interstitial Mn atoms can be roughly estimated to be $\sim 17\%$, assuming that flux peaking in the $\langle 110 \rangle$ channel of GaAs is ~ 1.5 .^{10,11,15} The presence of interstitials in the as-grown film is further confirmed in $\langle 110 \rangle$ and $\langle 111 \rangle$ planar channeling scans (not shown), where we observed a higher χ_{Mn} in the $\langle 111 \rangle$ as compared to that in the $\langle 110 \rangle$ 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 χ_{Mn} values 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 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 (nonmagnetic) heavily Be-doped LT GaAs. The ECV results are consistently within 10% of the Hall values of free-hole concentration.¹⁹ 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 $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ films.

The ion channeling and ECV results show that out of $\sim 2 \times 10^{21} \text{ cm}^{-3}$ Mn atoms in the as-grown $\text{Ga}_{0.91}\text{Mn}_{0.09}\text{As}$ only $6 \times 10^{20} \text{ cm}^{-3}$ 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 $\text{Mn}_i\text{-Mn}_{\text{Ga}}$ pairs and rendering Mn_{Ga} inactive as acceptors.

Annealing the sample at 282°C (only slightly above the growth temperature) breaks the relatively weak $\text{Mn}_i\text{-Mn}_{\text{Ga}}$ 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, $p = 1 \times 10^{21} \text{ cm}^{-3}$, 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 5 K on a number of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ 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 $\text{Mn}_i\text{-Mn}_{\text{Ga}}$ pairs, leading to a higher concentration of uncom-

compensated Mn spins. Note that, according to the ECV results, annealing increased the hole concentration p from $\sim 6 \times 10^{20} \text{ cm}^{-3}$ to $1 \times 10^{21} \text{ cm}^{-3}$ 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 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 the $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ alloy system. If so, this may be the reason why similar maximum values of T_C were found in $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ 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 $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ 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 antisite donors.^{24,25}

In conclusion, we have shown that the location of Mn sites in the $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ 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 $\text{III}_{1-x}\text{Mn}_x\text{V}$ alloys, are thus seen to be controlled by the behavior of unstable defects involving highly mobile Mn interstitials. In particular, the Curie temperature of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ 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 the maximum Curie temperature can be attributed to the limit on the free-hole concentration attainable in low-temperature-grown $\text{Ga}_{1-x}\text{Mn}_x\text{As}$.

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