Fundamental Curie Temperature Limit in Ferromagnetic Ga$_{1-x}$Mn$_x$As

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ABSTRACT

We provide experimental evidence that the upper limit of ~110 K commonly observed for the Curie temperature $T_C$ of Ga$_{1-x}$Mn$_x$As is caused by the Fermi-level-induced hole saturation. Ion channeling, electrical and magnetization measurements on a series of Ga$_{1-x-y}$Mn$_x$Be$_y$As layers show a dramatic increase of the concentration of Mn interstitials accompanied by a reduction of $T_C$ with increasing Be concentration, while the free hole concentration remains relatively constant at ~5x10$^{20}$ cm$^{-3}$. These results indicate that the concentrations of free holes and ferromagnetically active Mn spins are governed by the position of the Fermi level, which controls the formation energy of compensating interstitial Mn donors.

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The recent discovery of III-V ferromagnetic semiconductors, specifically Ga$_{1-x}$Mn$_x$As with Curie temperatures $T_C$ as high as 110 K [1-2] is a major step toward the implementation of spintronic devices for processing, transferring, and storing of information [3]. Experimentally it has been established that $T_C$ in Ga$_{1-x}$Mn$_x$As increases with increasing Mn concentration $x$ (as long as MnAs precipitates are not formed) and with hole concentration. Although each Mn atom in the Ga sublattice is expected to contribute a hole to the system, it was found that the hole concentration in this material is significantly lower than the Mn concentration (by a factor of 2-3) [1,2]. Recent ion channeling experiments demonstrated that such low Mn acceptor activation could be attributed to the presence of *interstitial Mn donors* in Ga$_{1-x}$Mn$_x$As [4].

Calculations based on the Zener model [5] predicted that $T_C$ in Ga$_{1-x}$Mn$_x$As could be improved by increasing the Mn content and/or the free hole concentration in the alloy. These predictions led to extensive experimental works aimed at achieving higher $T_C$ for Ga$_{1-x}$Mn$_x$As. Despite intense efforts, similar maximum values of $T_C$ of ~110K were found in thin Ga$_{1-x}$Mn$_x$As films prepared in different laboratories with rather different values of $x$, ranging from ~0.05 to 0.10 and optimally annealed at low temperatures in the range of 250-280ºC [2, 6-9]. A recent report by Potashnik *et al.* showed that in optimally annealed Ga$_{1-x}$Mn$_x$As alloys, the $T_C$ and conductivity saturate for $x > 0.05$ [8], suggesting that as $x$ increases, an increasing fraction of Mn spins do not participate in the ferromagnetism.

In an earlier post-growth annealing study of Ga$_{0.91}$Mn$_{0.09}$As films [4,9] we found that annealing at 280ºC for one hour increases $T_C$ from 65 K to 111 K and the hole concentration from $6 \times 10^{20}$ cm$^{-3}$ to $1 \times 10^{21}$ cm$^{-3}$. Ion channeling results demonstrated that this increase of both $T_C$ and the hole concentration can be attributed to the lattice site rearrangement of the highly unstable Mn interstitials Mn$_I$. These Mn$_I$ are expected to be highly mobile positively charged double donors [10,11]. They can, however, be immobilized by occupying the interstitial sites adjacent to the negatively-charged
substitutional Mn acceptors (MnGa), thus forming antiferromagnetically ordered MnI-MnGa pairs, which not only render MnGa inactive as acceptors, but also cancels its magnetic moment [4,10]. Low temperature annealing breaks up the relatively weak antiferromagnetically ordered MnI-MnGa pairs, leading to a higher concentration of uncompensated Mn spins, resulting in increase in saturation magnetization as well as a higher hole concentration and a higher T_C [4,6-9].

The above low temperature annealing results further suggested the possibility that there exists a fundamental limit on T_C, governed by a limit on the hole concentration allowed by the Ga_{1-x}Mn_xAs alloy [4]. In this paper we use co-doping of Ga_{1-x}Mn_xAs by Be as a tool to provide unambiguous experimental evidence that such a limit does in fact exist. It has been demonstrated that free hole concentration as high as 8x10^{20} cm^{-3} could be achieved in Be doped, low temperature grown GaAs [12]. We show that the free hole concentration \( p \) in Ga_{1-x-y}Mn_xBe_yAs with \( x=0.05 \) is nearly constant, independent of the Be doping level (up to \( y = 0.11 \)). In spite of this saturation of \( p \), we observe for a fixed Mn concentration of 0.05 a dramatic increase in the concentrations of MnI and of electrically inactive random Mn clusters at the expense of MnGa as the Be concentration is increased, accompanied by a strong decrease of T_C. These results strongly indicate that a Fermi-level-controlled mechanism puts an upper limit on T_C in Ga_{1-x}Mn_xAs [13].

Thin films of Ga_{1-x-y}Mn_xBe_yAs were grown on semi-insulating (001) GaAs substrates in a Riber 32 R&D MBE system. Prior to film 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 for the growth of a 3 nm thick low-temperature (LT) GaAs, followed by a 230 nm thick layer of Ga_{1-x-y}Mn_xBe_yAs at a substrate temperature of 270°C. The As\_2:Ga beam equivalent pressure ratio of 20:1 was maintained during the growth.

Magnetoresistance, Hall effect, and SQUID magnetometry were used for electrical and magnetic characterization of the samples and for determining T_C. Hall
effect measurements were performed in the Van der Pauw or the six-probe geometry. To circumvent the problems associated with the anomalous Hall effect (AHE) in ferromagnets [2, 14], we have used the electrochemical capacitance voltage (ECV) profiling method to measure the depth distribution of acceptors in our specimens. By comparing the Hall and ECV results on non-ferromagnetic Ga_{1-y}Be_{y}As thin films grown under similar conditions as the LT-Ga_{1-x}Mn_{x}As and Ga_{1-x-y}Be_{y}Mn_{x}As films, we have established that ECV can be reliably used to obtain the free hole concentration profiles in ferromagnetic LT-Ga_{1-x}Mn_{x}As [15].

The locations of Mn sites in the Ga_{1-x}Mn_{x}As lattice were studied by simultaneous channeling particle induced x-ray emission (c-PIXE) and Rutherford backscattering spectrometry (c-RBS) using a 1.95MeV \(^4\)He\(^+\) beam. Mn K\(_\alpha\) x-ray signals obtained by c-PIXE are directly compared with GaAs c-RBS signals coming from Ga_{1-x}Mn_{x}As films. The normalized yield for the RBS (\(\chi_{\text{GaAs}}\)) or the PIXE Mn x-ray signals (\(\chi_{\text{Mn}}\)) is defined as the ratio of the channeled yield to the corresponding unaligned “random” yield.

Figure 1 shows the PIXE and RBS angular scans (normalized yield as a function of the tilt angle around the channeling axis) about the <110> (taken along the \{110\} planar direction) and <111> axes for the Ga_{1-x}Mn_{x}As and Ga_{1-x-y}Be_{y}Mn_{x}As films with increasing y (results from only four out of six samples were shown for simplicity). The angular scans about the <100> directions are similar to those about the <111> direction for all samples and are therefore not shown. The total Mn content in all samples was determined by PIXE to be ~0.05. The Be contents was estimated from the lattice constant determined by x-ray diffraction that was calibrated by RHEED intensity oscillations.

For all the samples studied, the <111> axial Mn scans (c-PIXE) follow the host GaAs (RBS) scans, indicating that the dominant fraction of the Mn atoms are either on substitutional sites or are on specific sites shadowed by the host atoms [16,17]. This reveals that the majority of the Mn atoms is on specific (non-random) sites commensurate
with the lattice, but does not necessarily imply that all of the Mn atoms are in *substitutional* positions. At the same time the normalized yields $\chi_{Mn}$ in the <111> scans also shows a gradual increase, deviating from the corresponding host scans as the Be content increases, indicating an increase in Mn atoms in the form of random clusters not commensurate with the GaAs lattice.

In contrast to the <111> angular scans, the Mn <110> angular scans are strikingly different from their corresponding host scans in Fig. 1. In the sample without Be ($y = 0$), we observe that the <110> $\chi_{Mn}$ is significantly higher than that in the <111> scan, particularly in the middle of the channel, suggesting that a significant fraction of the non-random Mn shadowed in the <111> scans do not all occupy substitutional sites, and can thus be assumed to be located at the *interstitial* sites lying along the <111> axis of the zinc-blende crystal lattice. Atoms in these interstitial positions, tetrahedral or hexagonal in a diamond cubic lattice are shadowed by the host atoms when viewed along both the <100> and <111> axial directions. They are, however, exposed in the <110> axial channel [16,17], giving rise to a double-peak (tetrahedral site) or a single peak (hexagonal site) feature in the <110> angular scan due to the flux-peaking effect of the ion beam in that channel [16]. We find from the difference between the <110> and <111> scans for this sample that the fraction of Mn in interstitial sites amounts to ~7%.

As the Be content increases, the <110> Mn angular scans show a definite peak at the center of the channel that increases in intensity -- a clear signature for the presence of an increasing concentration of Mn interstitials in the alloy [18]. These results unambiguously reveal that the fraction of $Mn_I$ as well as random Mn-related clusters increases monotonically in Ga$_{1-x-y}$Be$_y$Mn$_x$As films with increasing Be content. The fractions of Mn atoms at the various sites -- substitutional ($Mn_{Ga}$), interstitial ($Mn_I$) and in random-cluster form ($Mn_{ran}$) -- as measured from the angular scans are shown in Fig. 2. Mn atoms in various lattice locations for a samples with $y \sim 0.03$ and 0.08 and annealed at 280ºC for 1 hr. are also shown. Notice that when the samples are annealed a dramatic
increase of Mn as random clusters at the expense of MnI is observed while the Mn_Ga fraction stays the same revealing the relative instability of the MnI.

Figure 3 shows the free hole concentration obtained from ECV and Hall measurements together with the Curie temperature $T_C$ for as-grown samples with different Be content $y$. It is particularly worth noting that $T_C$ of the Ga$_{1-x-y}$Mn$_x$Be$_y$As films drops rapidly as $y$ increases – in fact the samples become non-ferromagnetic for $y > 0.05$ -- while the free hole concentration measured by ECV remains rather constant throughout the entire Be composition range. We point out that for the ferromagnetic Ga$_{1-x}$Mn$_x$As thin film where the $T_C$ is high a large discrepancy in the hole concentration measured by Hall effect is observed due to the strong AHE even at room temperature. As the Be concentration in the film increases ($y > 0.05$), the Ga$_{1-x-y}$Mn$_x$Be$_y$As films lose their ferromagnetic property and the hole concentrations measured by Hall effect is seen to approach that measured by the ECV method.

The ECV data show that the different Ga$_{1-x-y}$Be$_y$Mn$_x$As films have similar values of free hole concentration of $\sim 4$ to $6 \times 10^{20}/\text{cm}^3$. It has been established that in compound semiconductors the carrier concentration is limited by the formation of compensating native defects. The formation energies of these defects are governed by the position of the Fermi level [19,20]. The relatively constant hole concentration of about $5 \times 10^{20}/\text{cm}^3$ shown in Fig. 3 indicates that the hole concentration in these Ga$_{1-x-y}$Mn$_x$Be$_y$As samples is at the free hole saturation limit $p_{\text{max}}$. As this limit is reached, the formation energies of Mn$_{Ga}$ acceptors and compensating MnI become comparable. Introduction of additional Be acceptors into the Ga$_{1-x-y}$Mn$_x$Be$_y$As samples then leads to a downward shift of the Fermi energy, that in turn increases the formation energy of negatively charged Mn$_{Ga}$ acceptors. As a result, an increasing fraction of Mn is incorporated in the form of MnI donors and/or electrically inactive MnAs or Mn clusters [21]. The creation of MnI not only puts a limit on the maximum hole concentration, but also has a profound effect on
the number of ferromagnetically active spins and -- for a constant hole concentration -- on the RKKY coupling of these spins.

Specifically, there are three mechanisms to note in this context. First, it has been shown theoretically that Mn_I on tetrahedral sites do not participate in the RKKY-mediated ferromagnetism because Mn_I d-orbitals do not hybridize with the p-states of the holes at the top of the valence band [10]. Second, as mentioned earlier, the Mn_I donors may form antiferromagnetically ordered Mn_I-Mn_Ga pairs [10], which not only renders Mn_Ga inactive as acceptors, but also reduces the total number of uncompensated Mn spins participating in the ferromagnetism. Such drop in the number of active spins reduces T_C. Finally, when the number of active spins becomes approximately equal to the hole concentration, the average distance between the active Mn spins becomes larger than the first node in the oscillatory RKKY exchange coupling (at \( \approx 1.17 \ r_{\text{hole}} \), where \( r_{\text{hole}} \) is the average distance between holes [22]). In this situation some Mn_Ga ions may couple antiferromagnetically between themselves. This would at first lead to the drop in T_C, and eventually should drive the system into a spin-glass state [22-24]. We believe that some or all of the above factors contribute to the strong drop in T_C and to the disappearance of ferromagnetism in Ga_{1-x-y}Mn_xBe_yAs with increasing Be content.

In conclusion, our present work on LT- Ga_{1-x-y}Mn_xBe_yAs alloys, together with previously reported studies of the low temperature annealing of Ga_{1-x}Mn_xAs, reveal that the ferromagnetism in Ga_{1-x}Mn_xAs is related to the total number of uncompensated Mn ions, which are in turn controlled by the formation energies of compensating native defects. As the Mn concentration x increases beyond the doping limit \( p_{\text{max}} \), it is energetically favorable to form compensating Mn_I, thus keeping the product of the free hole concentration and of the concentration of the net uncompensated Mn spins participating in the ferromagnetism relatively constant at the maximum level. Given that the ferromagnetism in this system is related to the uncompensated Mn spins and is mediated by holes, such Fermi-level-induced hole saturation effect necessarily imposes a
fundamental limit on the Curie temperature of the system. Since the total number of acceptors has to be maintained below $p_{\text{max}}$, co-doping of Ga$_{1-x}$Mn$_x$As with Be acceptors creates a huge increase of Mn$_I$, thus killing ferromagnetism. This experimental observation leads us to propose using heavy n-type counter-doping of Ga$_{1-x}$Mn$_x$As (with, e.g., Te) as a remedy for the otherwise unavoidable creation of Mn interstitials at higher values of $x$. In such Ga$_{1-x}$Mn$_x$Te$_z$As$_{1-z}$ it should be possible to achieve values of $x \approx p_{\text{max}}+z$. Although the hole concentration will still be “pinned” at $p_{\text{max}}$ by the limit imposed on the Fermi level, the number of active Mn would increase in proportion to $x$, thus increasing $T_C$.

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This paper addresses the thermodynamic $T_C$ limit for uniform $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ films and that the $T_C$ limit of about 110K may deviate depending on the growth and annealing conditions. Hence this temperature cannot be viewed as a “hard” limit for all GaMnAs based structures. For example $T_C$ of as high as 140K has been suggested by Edmonds et al. (http://arXiv.org/abs/cond-mat/0209554) for thin $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ layers (~45nm) annealed at very low temperature (180ºC) for as long
as 230 hours. Surface and/or interface effects are expected to play an important role in this case. Some improvements on $T_C$ have been also achieved by Ohno et al in Be co-doped double layer structures. However, considerations of the thermodynamic equilibrium in such nonuniform systems are beyond the scope of this article.

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FIGURE CAPTION

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

Fig. 2  The fractions of Mn atoms at the various sites -- substitutional ($\text{Mn}_\text{Ga}$), interstitial ($\text{Mn}_\text{i}$) and in random-cluster form ($\text{Mn}_\text{ran}$) -- as measured from the angular scans shown in Fig. 1. The Mn fractions for the sample with $y\sim0.08$ annealed at $280^\circ\text{C}$ for 1 hr. are also shown as closed symbols.

Fig. 3  The hole concentrations determined by ECV and Hall measurements and the Curie temperatures $T_C$ for as-grown $\text{Ga}_{1-x-y}\text{Mn}_x\text{Be}_y\text{As}$ films with increasing Be content $y$. 
Fig. 2
Fig. 3

-hole concentration (cm$^{-3}$)
-Be content, $y$
-Curie temperature, $T_C$ (K)

- holes (ECV)
- hoels (Hall)