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Curie temperature limit in ferromagnetic $Ga_{1-x}Mn_xAs$

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We provide experimental evidence that the upper limit of ~110 K commonly observed for the Curie temperature T_C of $Ga_{1-x}Mn_xAs$ thin films (thickness >50 nm) is caused by Fermi-level-induced hole saturation. Ion channeling, electrical, and magnetization measurements on a series of $Ga_{1-x-y}Mn_xBe_yAs$ 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 $\sim 5 \times 10^{20}$ 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 $Ga_{1-x}Mn_xAs$ with Curie temperatures T_C as high as 110 K (Refs. 1 and 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 $Ga_{1-x}Mn_xAs$ 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* (Mn_I) *double donors* in $Ga_{1-x}Mn_xAs$.[4] We have compared the net uncompensated Mn acceptors ($[Mn_{Ga}]$-$2x[Mn_I]$) and free hole concentration for $Ga_{1-x}Mn_xAs$ samples with x ranging from 0.02 to 0.09. Our results revealed that the free-hole concentration can be well explained by compensation of Mn_{Ga} acceptors by Mn_I double donors for samples with $x<0.05$. For samples with $x>0.05$, compensation by Mn_I alone cannot fully account for the low hole concentration. In this case, As antisite (As_{Ga}) donors can also compensate some of the substitutional Mn acceptors.[5] These results suggest that high Mn contents in GaAs (substitutional and/or interstitial) may also promote the formation of As_{Ga}.

Calculations based on the Zener model[6] predicted that T_C in $Ga_{1-x}Mn_xAs$ 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 $Ga_{1-x}Mn_xAs$. Despite intense efforts, similar maximum values of T_C of ~110 K were found in thin $Ga_{1-x}Mn_xAs$ films with thickness >50 nm 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 250–280 °C.[2,7–10] A recent report by Potashnik *et al.* showed that in optimally annealed $Ga_{1-x}Mn_xAs$ alloys, the T_C and conductivity saturate for $x>0.05$,[9] 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[4,10] we found that annealing at 280 °C for 1 h increases T_C from 65 to 111 K and the hole concentration from 6×10^{20} to 1×10^{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.[11,12] They can, however, be immobilized by occupying the interstitial sites *adjacent* to the negatively charged substitutional Mn acceptors (Mn_{Ga}), thus forming antiferromagnetically ordered Mn_I-Mn_{Ga} pairs, which not only render Mn_{Ga} inactive as acceptors, but also cancel its magnetic moment.[4,11] Low-temperature annealing breaks up the relatively weak antiferromagnetically ordered Mn_I-Mn_{Ga} pairs, leading to a higher concentration of uncompensated Mn spins, resulting in an increase in saturation magnetization as well as a higher hole concentration and a higher T_C.[4,7–10] Since it has been reported that As_{Ga} defects were stable up to 450 °C,[13] they cannot be responsible for the low-temperature annealing-induced improvements.[5,7]

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 codoping 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 concentrations as high as 8×10^{20} cm^{-3} could be achieved in Be-doped, low-temperature-grown GaAs.[14] 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

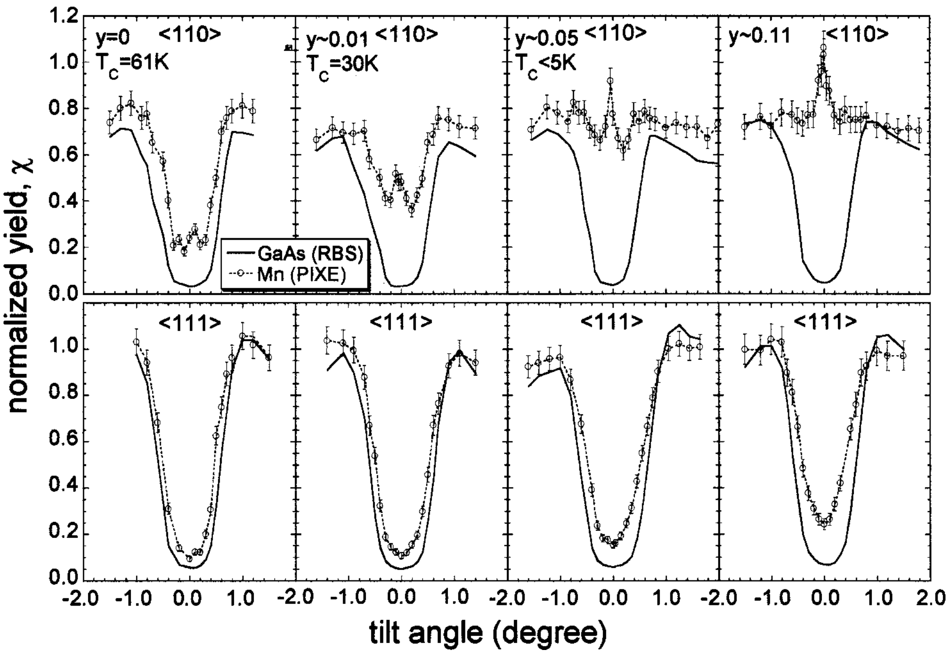

FIG. 1. Angular scans about the ⟨110⟩ and ⟨111⟩ axes for undoped and Be-doped $Ga_{1-x}Mn_xAs$ samples. The ⟨110⟩ angular scans are taken along the {110} planar channel.

fixed Mn concentration of 0.05 a dramatic increase in the concentrations of Mn_I and electrically inactive random Mn clusters at the expense of Mn_{Ga} 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 $Ga_{1-x}Mn_xAs$.[15]

Thin films of $Ga_{1-x-y}Mn_xBe_yAs$ were grown on semi-insulating (001) GaAs substrates in a Riber 32 R&D molecular beam epitaxy (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 superconducting quantum interference device (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 six-probe geometry. To circumvent the problems associated with the *anomalous Hall effect* (AHE) in ferromagnets,[2,16] 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 nonferromagnetic $Ga_{1-y}Be_yAs$ thin films grown under similar conditions as the LT $Ga_{1-x}Mn_xAs$ and $Ga_{1-x-y}Be_yMn_xAs$ films, we have established that ECV can be reliably used to obtain the free-hole concentration profiles in ferromagnetic LT $Ga_{1-x}Mn_xAs$.[17]

The locations of Mn sites in the $Ga_{1-x}Mn_xAs$ lattice were studied by simultaneous channeling-particle-induced x-ray emission (c-PIXE) and Rutherford backscattering spectrometry (c-RBS) using a 1.95-MeV $^4He^+$ beam. Mn $K\alpha$ x-ray signals obtained by c-PIXE are directly compared with GaAs c-RBS signals coming from $Ga_{1-x}Mn_xAs$ films. 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 "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 $Ga_{1-x}Mn_xAs$ and $Ga_{1-x-y}Be_yMn_xAs$ films with increasing y (results from only four out of six samples are 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 content was estimated from the lattice constant determined by x-ray diffraction that was calibrated by reflection high-energy electron diffraction (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.[18,19] This reveals that the majority of the Mn atoms are on specific (nonrandom) sites commensurate with the lattice, but that does not necessarily imply that all of the Mn atoms are in *substitutional* positions. At the same time the normalized yields χ_{Mn} in the ⟨111⟩ scans also show 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⟩ χ_{Mn} is significantly higher than that in the ⟨111⟩ scan, particularly in the middle of the channel, suggesting that a significant fraction of the nonrandom 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

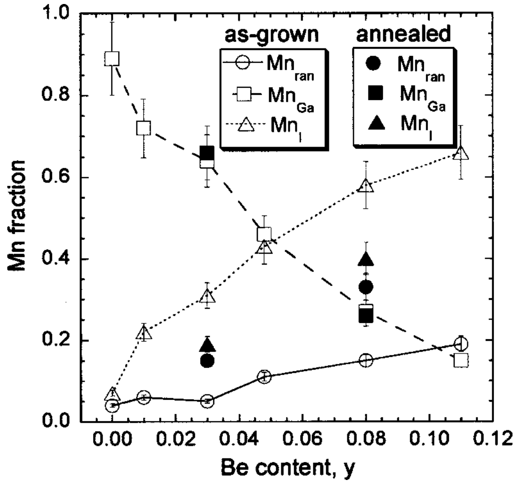

FIG. 2. Fractions of Mn atoms at the various sites—substitutional (Mn_{Ga}), interstitial (Mn_I), and in random-cluster form (Mn_{ran})—as measured from the angular scans shown in Fig. 1. The Mn fractions for the sample with $y\sim0.03$ and 0.08 annealed at 280 °C for 1 h are also shown as solid symbols.

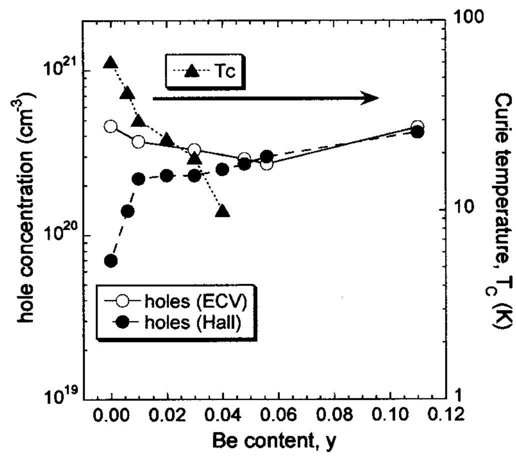

FIG. 3. Hole concentrations determined by ECV and Hall measurements and the Curie temperatures T_C for as-grown $Ga_{1-x-y}Mn_xBe_yAs$ films with increasing Be content y.

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,[18,19] 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.[18] 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.[20] These results unambiguously reveal that the fraction of Mn_I as well as random Mn-related clusters increases monotonically in $Ga_{1-x-y}Be_yMn_xAs$ 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 $y\sim0.03$ and 0.08 and annealed at 280 °C for 1 h are also shown. Notice that when the samples are annealed a dramatic increase of Mn as random clusters at the expense of Mn_I is observed while the Mn_{Ga} fraction stays the same, revealing the relative instability of the Mn_I.

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 $Ga_{1-x-y}Mn_xBe_yAs$ films drops rapidly as y increases—in fact the samples become nonferromagnetic 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 $Ga_{1-x}Mn_xAs$ 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 $Ga_{1-x-y}Mn_xBe_yAs$ films lose their ferromagnetic property and the hole concentration measured by Hall effect is seen to approach that measured by the ECV method.

The ECV data show that the different $Ga_{1-x-y}Be_yMn_xAs$ films have similar values of the free-hole concentration of $\sim4-6\times10^{20}/cm^3$. 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.[21,22] The relatively constant hole concentration of about $5\times10^{20}/cm^3$ shown in Fig. 3 indicates that the hole concentration in these $Ga_{1-x-y}Mn_xBe_yAs$ samples is at the free-hole saturation limit p_{max}. As this limit is reached, the formation energies of Mn_{Ga} acceptors and compensating Mn_I become comparable. The introduction of additional Be acceptors into the $Ga_{1-x-y}Mn_xBe_yAs$ samples then leads to a downward shift of the Fermi energy, which 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 Mn_I donors and/or electrically inactive MnAs or Mn clusters.[23] The creation of Mn_I 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 a 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 $\approx 1.17 r_{hole}$, where r_{hole} is the average distance between holes).[24] In this situation some Mn_{Ga} ions may couple antiferromagnetically between themselves. This would at first lead to a drop in T_C and, eventually, should drive the system into a spin-glass state.[24–26] 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 $Ga_{1-x}Mn_xAs$, reveals 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_{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 a 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_{max}, codoping of $Ga_{1-x}Mn_xAs$ with Be acceptors creates a huge increase of Mn_I, thus destroying ferromagnetism. This experimental observation leads us to propose using *heavy n-type counter doping* of $Ga_{1-x}Mn_xAs$ (with, e.g., Te) as a remedy for the otherwise unavoidable creation of Mn interstitials at higher values of x. In such $Ga_{1-x}Mn_xTe_zAs_{1-z}$ it should be possible to achieve values of $x \approx p_{max}+z$. Although the hole concentration will still be "pinned" at p_{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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