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Publication Date

2004-01-30

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Direct Evidence of the Fermi-Energy-Dependent Formation of Mn Interstitials in Modulation Doped $Ga_{1-y}Al_yAs/Ga_{1-x}Mn_xAs/Ga_{1-y}Al_yAs$ Heterostructures

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ABSTRACT

Using ion channeling techniques, we investigate the lattice locations of Mn in $Ga_{1-x}Mn_xAs$ quantum wells between Be-doped $Ga_{1-y}Al_yAs$ barriers. Our earlier results showed that the Curie temperature T_C depends on the *growth sequence* of the epitaxial layers. A lower T_C was found in heterostructures in which the $Ga_{1-x}Mn_xAs$ layer is grown *after* the modulation-doped barrier. Here we provide direct evidence that this reduction in T_C is directly correlated with an increased formation of magnetically inactive Mn interstitials. The formation of interstitials is induced by a shift of the Fermi energy as a result of the transfer of holes from the barrier to the quantum well during the growth.

PACS numbers: 75.50.Pp, 72.80.Ey, 73.61.Ey, 75.70.-I

The recent success in the growth of $In_{1-x}Mn_xAs$ and $Ga_{1-x}Mn_xAs$ with relatively high ferromagnetic transition temperatures T_C has stimulated renewed interests in diluted magnetic semiconductors (DMSs) [1, 2], largely due to their potential for spintronics applications. It has been generally accepted that the ferromagnetic interaction in the III-V DMSs is mediated by free holes [3]. Mean field theory further predicts that the value of T_C should scale as the product of the Mn concentration and the third root of the hole density [3].

By combining ion channeling studies (to determine the Mn ion location in the lattice) and electrochemical capacitance-voltage (ECV) profiling (to determine the free hole concentration), we have recently found that a fraction of Mn ions in $Ga_{1-x}Mn_xAs$ is located in interstitial positions (Mn_I) [4, 5]. We have further demonstrated that the formation of Mn_I is responsible for the saturation of ferromagnetism in $Ga_{1-x}Mn_xAs$. Since Mn_I are double donors, they reduce the hole concentration by compensating substitutional Mn_{Ga} acceptors. Moreover, the spins of isolated Mn_I do not contribute to ferromagnetism because of their negligible *p-d* exchange hybridization [6]. Mn_I may also tend to form antiferromagnetic Mn_I-Mn_{Ga} pairs, thus canceling the magnetic moment of Mn_{Ga} [6]. The recent intriguing reports on the improvement of ferromagnetism in $Ga_{1-x}Mn_xAs$ after low temperature annealing [7-11] is explained rather well by thermally activated removal of these Mn interstitials [4].

Our experiments on Be doped $Ga_{1-x}Mn_xAs$, in which the concentration of spins and holes can be independently controlled, have clearly suggested that the commonly observed limits on T_C in $Ga_{1-x}Mn_xAs$ originates from a *Fermi-level-governed* transfer of Mn atoms from their magnetically-active substitutional acceptor sites to magnetically-inactive or compensating interstitial donor sites [12]. Specifically, we showed that an increase of the free hole concentration through Be doping leads to an increase in the fraction of Mn atoms transferred from substitutional to interstitial sites, thus resulting in a lower Curie temperature [12].

Recently an alternative approach has been proposed to control the T_C of $Ga_{1-x}Mn_xAs$, by using modulation doping of $Ga_{1-y}Al_yAs/Ga_{1-x}Mn_xAs/Ga_{1-y}Al_yAs$ heterostructures. Briefly, the Mn concentration in the $Ga_{1-x}Mn_xAs$ quantum well is kept constant in this approach, while the hole density in the well is controlled through *p*-type doping of the $Ga_{1-y}Al_yAs$ barrier [13, 14]. It was shown that introducing Be acceptors into the $Ga_{1-y}Al_yAs$ barriers in all low-temperature-grown $Ga_{1-y}Al_yAs/Ga_{1-x}Mn_xAs/Ga_{1-y}Al_yAs$ QW structures leads to an increase of T_C from 70 K in undoped heterostructure to over 100 K in modulation doped heterostructure (MDH) [13]. Also it has been observed that T_C strongly depends on the MDH growth sequence. Using Be doping in only one of the two $Ga_{1-y}Al_yAs$ barriers, higher T_C's were found in so-called normal MDHs (N-MDHs), in which the $Ga_{1-x}Mn_xAs$ wells were grown first, followed by the growth of the Be-doped barrier. In contrast, significantly lower T_C's were found in *inverted* MDHs (I-MDHs), in which the modulation doped barrier was grown first, followed by the quantum well. It was suggested [13] that in I-MDH holes transferred from the barrier lower the Fermi energy level during the growth of the $Ga_{1-x}Mn_xAs$, causing an increase in the concentration of the compensating Mn_I, and thus lowering the T_C.

By investigating the formation of Mn interstitials via ion channeling in modulation doped $Ga_{1-x}Mn_xAs$ heterostructures, we provide direct experimental evidence that the formation of these interstitials is *directly controlled by the Fermi energy*. Specifically, we observe a significantly higher concentration of Mn_I in I-MDH, i.e., that exhibiting a lower T_C. This observation is in full agreement with the Fermi-level-induced limitation of T_C in $Ga_{1-x}Mn_xAs$, thus providing additional strong support for this model [12]. This also rules out the possibility of other effects, such as the competition between Mn and Be atoms to occupy the same substitutional site, since in modulation-doped structures Mn and Be atoms are spatially separated.

Two $Ga_{0.76}Al_{0.24}As/Ga_{1-x}Mn_xAs/Ga_{0.76}Al_{0.24}As$ heterostructures with Be doping in *one* of the two barriers – deposited either before the QW (I-MDH) or after the QW (N-

MDH) -- were investigated. In addition, we also studied a heterostructure in which both barriers were undoped. In all cases the width of the QW was 5.6 nm, the value of x in the well was 0.062, and the total thickness of each barrier was 13.5 nm. Details of the growth conditions were reported elsewhere [13]. Both the $Ga_{1-y}Al_yAs$ and $Ga_{1-x}Mn_xAs$ layers in the MDHs were grown at the same low temperature of 210ºC. The Be concentration in the doped $Ga_{1-y}Al_yAs$ was controlled by the temperature of the Be cell T_{Be}, and was estimated to be $\sim 6\times10^{20}cm^{-3}$ [12]. Hall measurements on thick (d = 98nm) $Ga_{0.76}Al_{0.24}As$:Be layers grown at 210 ºC with the same Be flux gave $p = 2.8\times10^{20}$ cm^{-3} [13]. Resistivity, Hall effect, and SQUID measurements were used for electrical and magnetic characterization of the samples, and for determining T_C as reported earlier [13].

The lattice locations of the Mn atoms in the $Ga_{1-x}Mn_xAs$ QW were studied by simultaneous Rutherford backscattering spectrometry (RBS) and particle induced x-ray emission (PIXE) measurements using a 1.95MeV $^4He^+$ beam. Backscattered He ions and characteristic x-rays excited by the He ions were detected by a Si surface barrier detector located at a backscattering angle of 165° and a Si(Li) detector located at 30°, respectively, with respect to the incident ion beam. The specific locations of Mn atoms in the $Ga_{1-x}Mn_xAs$ lattice were determined by directly comparing the angular scans about the <110> and <111> axial channels of the Mn K_α x-ray signals (PIXE) with those of the RBS signals of GaAs from the $Ga_{1-x}Mn_xAs$ QW. Due to the small total Mn content in all of the samples ($<8x10^{14}cm^{-2}$), a total charge of 20 μC was accumulated for each channeling spectrum.

Figure 1 shows the temperature dependence of normalized magnetization obtained from the Arrot plot analysis of the anomalous Hall effect data for N-MDH, I-MDH and the undoped heterostructures. In the analysis the side-jump scattering mechanism was assumed to be dominant in the AHE [2]. The values of T_C as measured by temperature dependence of the SQUID remanent magnetization are also shown and marked with arrows [13]. This method of accessing the Be-doping-induced variation of the magnetic properties of heterostructes is in good agreement with our previously published results obtained from resistivity and SQUID magnetization measurements [13]. As compared to T_C = 80 K for the undoped heterostructure, we find that T_C increases to 98 K for the N-MDH and decreases to 70 K for the I-MDH. We have argued earlier that this distinct behavior, expected on the basis of our previous experiments on Be co-doping [12], is related to the Fermi-level-induced increase in the concentration of Mn_I in I-MDH [13].

Figure 2 shows the normalized yields of the Mn (PIXE) and GaAs (RBS) signals from the $Ga_{1-x}Mn_xAs$ QW for both the I-MDH and N-MDH as functions of the incident beam angles about the <110> and <111> axes (angular scans). The normalized yield for the RBS (χ_{GaAs}) and for the PIXE Mn x-ray signals (χ_{Mn}) are defined as the ratio of the channeled yield to the corresponding unaligned yield. We note that atoms in the interstitial positions (tetrahedral or hexagonal) in a diamond lattice are shadowed by the host atoms when viewed along both the <100> and <111> axial channels, but are exposed in the <110> axial channel [15]. In Fig. 2, the χ_{Mn} for both samples follows the χ_{GaAs} host very well in the <111> scans. This indicates that most of the Mn atoms are shadowed by the Ga and As host atoms. However it does not necessarily mean that they occupy substitutional sites in the lattice. The slightly higher χ_{Mn} in the <111> direction for both samples suggests that a small fraction (<10%) of Mn is in random positions not commensurate with the lattice. These random Mn atoms are most probably present as small clusters of Mn or MnAs [4].

On the other hand, the χ_{Mn} values for both samples in the <110> scans are clearly higher than those in the <111> scans. This is similar to the case for thicker $Ga_{1-x}Mn_xAs$ layers, where we interpreted this as an unambiguous signature for the presence of *interstitial* Mn atoms Mn_I [4,12]. The difference in the Mn lattice location between the I-MDH and N-MDH is illustrated in the Mn angular scans about the <110> axial channel shown in Fig. 2. The much higher χ_{Mn} in the <110> scan for the I-MDH indicates that the concentration of Mn_I is higher in the $Ga_{1-x}Mn_xAs$ QW when the Be-doped barrier layer is grown prior to the deposition of the QW. Assuming a flux peaking in the <110> channel to be ~1.5-2.0 [4], we estimate the fractions of Mn_I to be ~20% for I-MDH and ~11% for N-MDH. We note that the angular scans of the undoped heterostructure (not shown) are similar to the N-MDH within experimental error.

The channeling results provide the explanation for the degradation of ferromagnetism in I-MDHs, as revealed by electrical transport and magnetization measurements. In I-MDH the $Ga_{1-x}Mn_xAs$ QW is grown in the presence of free holes transferred from the Be-doped barrier that is already in place during the $Ga_{1-x}Mn_xAs$ deposition. As has been argued earlier [12], when the hole density is sufficiently high, the Fermi level reaches a saturation value, and beyond that point it is energetically more favorable for Mn atoms to incorporate into interstitial – rather than substitutional – sites [16] *during the growth*, resulting in degradation of ferromagnetism in $Ga_{1-x}Mn_xAs$. The case of I-MDH thus resembles the instance of previously studied $Ga_{1-x}Mn_xAs$ layers doped with Be acceptors [12], where it was shown that in $Ga_{1-x}Mn_xAs$ with hole concentrations close to the saturation limit the additional holes from Be acceptors had a detrimental effect on the T_C. In fact at sufficiently high Be doping levels the ferromagnetic coupling was be completely eliminated [12].

Apart from providing an explanation for differences in the magnetic properties in different $Ga_{1-x}Mn_xAs$-based heterostructures, our present study also has general implications for understanding defect formation during epitaxial growth. It clearly shows that the formation of defects can be affected by the growth sequence, thus providing a handle for controlling the properties of epitaxial structures. For example, the present results provide direct support for the previously advanced explanation of differences in maximum mobility in the 2-dimensional electron gas in inverted and normal GaAs/AlGaAs MDHs [17]. It has been argued in that context that the lower electron mobility in n-type I-MDH results from a higher concentration of acceptor-like native defects. The formation of these defects is induced by the upward shift of the Fermi energy resulting from a transfer of electrons from the n-type modulation doped AlGaAs barrier to the GaAs quantum well.

In conclusion, we have shown that in modulation-doped $Ga_{1-y}Al_yAs/Ga_{1-x}Mn_xAs/Ga_{1-y}Al_yAs$ heterostructures the ratio of the Mn_I donors to Mn_{Ga} acceptors depends on the growth sequence of the $Ga_{1-x}Mn_xAs$ quantum well and the Be-doped $Ga_{1-y}Al_yAs$ barrier. The Fermi-level-induced reduction of the formation energy of Mn_I provides a clear explanation for the trends in the T_C observed in normal and inverse modulation-doped heterostructures.

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Science Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098; NSF Grant DMR02-10519 and the DARPA SpinS Program under ONR grant N00014-00-1-0951

REFERNCES

1. H. Ohno, Science **281**, 951 (1998).

2. H. Ohno, J. Mag. Mag. Mat. **200**, 110 (1999) and references therein

3. T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science **287,** 1019 (2000).

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

5. K. M. Yu, W. Walukiewicz, T. Wojtowicz, W.L. Lim, X. Liu, Y. Sasaki, M. Dobrowolska, and J.K. Furdyna, Appl. Phys. Lett. **81**, 845 (2002).

6. J. Blinowski and P. Kacman, Phys. Rev. B **67**, 121204(R) (2003).

7. S. J. Potashnik, K. C. Ku, S. H. Chun, J. J. Berry, N. Samarth, and P. Schiffer, Appl. Phys. Lett. **79**, 1495 (2001).

8. S. J. Potashnik, C. K. Ku, R. Mahendiran, S. H. Chun, R. F. Wang, N. Samarth, and P Schiffer, Phys. Rev. **B66**, 012408 (2002).

9.K. W. Edmonds, K. Y. Wang, R. P. Campion, A. C. Neumann, N. R. S. Farley, B. L. Gallagher, and C. T. Foxon, Appl. Phys. Lett. **81**, 4991 (2002).

10. D. Chiba, K. Takamura, F. Matsukura, and H. Ohno, Appl. Phys. Lett. 82, 3020 (2003).

11. K. C. Ku, S. J. Potashnik, R. F. Wang, S. H. Chun, P. Schiffer, N. Samarth, M. J. Seong, A. Mascarenhas, E. Johnston-Halperin, R. C. Myers, A. C. Gossard, and D. D. Awschalom, Appl. Phys. Lett. 82, 2302 (2003).

12. K. M. Yu, W. Walukiewicz, T. Wojtowicz, W. L. Lim, X. Liu, Y. Sasaki, M. Dobrowolska, and J. K. Furdyna, Phys. Rev. B **68**, 041308-1(R) (2003).

13. T. Wojtowicz, W.L. Lim, X. Liu, M. Dobrowolska, J. K. Furdyna, K. M. Yu, W. Walukiewicz, I. Vurgaftman, and J. R. Meyer, Appl. Phys. Lett. **83**, 4220 (2003).

14. A. M. Nazmul, S. Sugahara, and M. Tanaka, Phys. Rev. B **67**, 241308-1(R) (2003).

15. L. Feldman, J. W. Mayer, and S. T. Picraux, *Materials Analysis by Ion Channeling* (Academic, New York, 1982).

16. Priya Mahadevan and Alex Zunger, Phys. Rev. B68, 075202 (2003).

17. W. Walukiewicz, and E. E. Haller, Appl. Phys. Lett., **58**, 1638 (1991).

FIGURE CAPTION

Fig. 1 Temperature dependence of normalized magnetization obtained from the Arrot plot analysis of the anomalous Hall effect data in three $Ga_{0.76}Al_{0.24}As/Ga_{1-x}Mn_xAs/Ga_{0.76}Al_{0.24}As$ quantum well structures. – Be acceptors were introduced either into the first barrier grown *before* the QW (I-MDH), or into the second barrier, grown after the QW (N-MDH). The "undoped" sample represents the heterostructure with no doping in either of the barriers. Lines are guides for the eye.

Fig. 2 Normalized yields of the Mn (PIXE) and GaAs (RBS) signals from the $Ga_{1-x}Mn_xAs$ QW for both I-MDH and N-MDH as a function of the incident tilt angles about the <110> and <111> axes (angular scans).

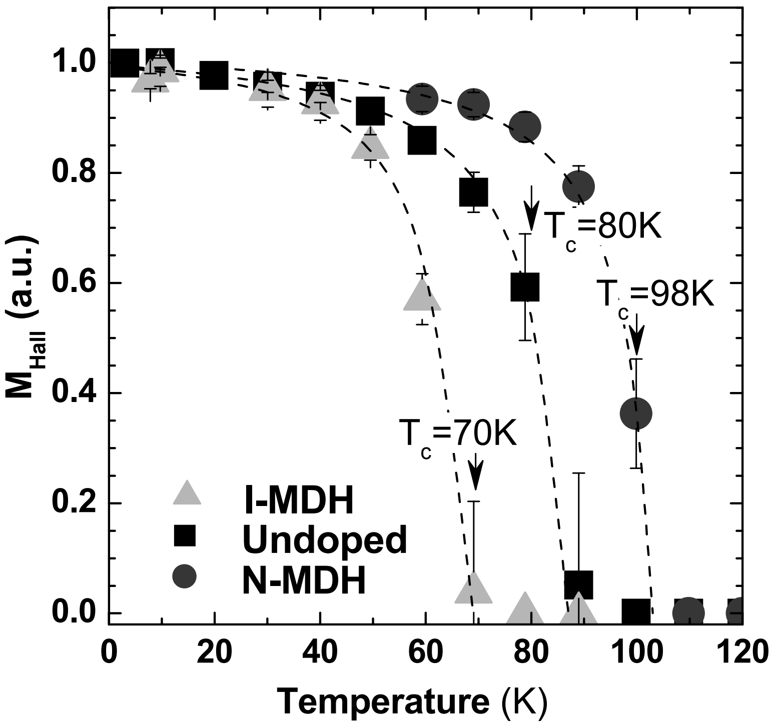
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
100
120
M_Hall (a.u.)
Temperature (K)
T_c=80K
T_c=98K
T_c=70K
I-MDH
Undoped
N-MDH

Fig. 1

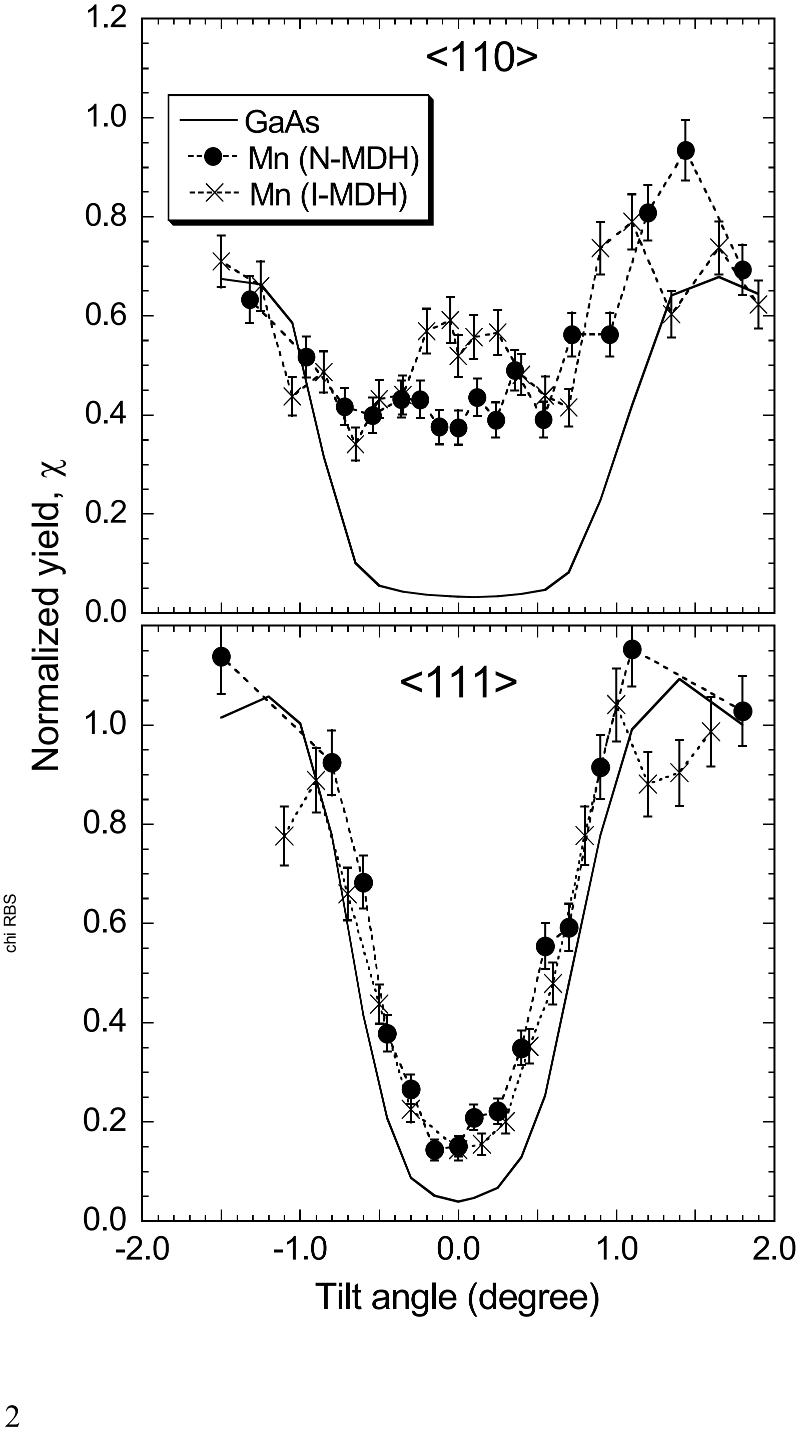
<110>
GaAs
Mn (N-MDH)
Mn (I-MDH)
<111>
Normalized yield, χ
chi RBS
Tilt angle (degree)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
-2.0
-1.0
0.0
1.0
2.0

Fig. 2