Title
Direct evidence of the fermi-energy-dependent formation of Mn interstitials in modulation doped Ga1-yAlyAs/Ga1-xMnxAs/Ga1-yAlyAs heterostructures

Permalink
https://escholarship.org/uc/item/0zg1t63v

Authors
Yu, K.M.
Walukiewicz, W.
Wojtowicz, T.
et al.

Publication Date
2004-01-30

Peer reviewed
Direct Evidence of the Fermi-Energy-Dependent Formation of Mn Interstitials in Modulation Doped Ga$_{1-x}$Al$_x$As/Ga$_{1-x}$Mn$_x$As/Ga$_{1-y}$Al$_y$As Heterostructures

K. M. Yu and W. Walukiewicz

Electronic Materials Program, Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

T. Wojtowicz,

Department of Physics, University of Notre Dame, Notre Dame, IN 46556 and Institute of Physics, Polish Academy of Sciences, 02-668 Warsaw, Poland

W.L. Lim, X. Liu, M. Dobrowolska, and J. K. Furdyna

Department of Physics, University of Notre Dame, Notre Dame, IN 46556

ABSTRACT

Using ion channeling techniques, we investigate the lattice locations of Mn in Ga$_{1-x}$Mn$_x$As quantum wells between Be-doped Ga$_{1-y}$Al$_y$As 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$_x$As 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$_x$As and Ga$_{1-x}$Mn$_x$As 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$_x$As 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$_x$As. 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$_x$As 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$_x$As, 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$_x$As 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$_x$As, by using modulation doping of Ga$_{1-y}$Al$_y$As/Ga$_{1-x}$Mn$_x$As/Ga$_{1-y}$Al$_y$As heterostructures. Briefly, the Mn concentration in the Ga$_{1-x}$Mn$_x$As 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$_y$As barrier [13, 14]. It was shown that introducing Be acceptors into the Ga$_{1-y}$Al$_y$As barriers in all low-temperature-grown Ga$_{1-y}$Al$_y$As/Ga$_{1-x}$Mn$_x$As/Ga$_{1-y}$Al$_y$As 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$_y$As barriers, higher $T_C$’s were found in so-called normal MDHs (N-MDHs), in which the Ga$_{1-x}$Mn$_x$As 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$_x$As, causing an increase in the concentration of the compensating Mn$_{II}$, and thus lowering the $T_C$.

By investigating the formation of Mn interstitials via ion channeling in modulation doped Ga$_{1-x}$Mn$_x$As 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$_{II}$ 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$_x$As, 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$_x$As/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$_{1-x}$Al$_x$As and Ga$_{1-x}$Mn$_x$As layers in the MDHs were grown at the same low temperature of 210ºC. The Be concentration in the doped Ga$_{1-x}$Al$_x$As was controlled by the temperature of the Be cell $T_{Be}$, and was estimated to be $\sim 6 \times 10^{20}$ cm$^{-3}$ [12]. Hall measurements on thick ($d = 98$ nm) Ga$_{0.76}$Al$_{0.24}$As:Be layers grown at 210 ºC with the same Be flux gave $p = 2.8 \times 10^{20}$ 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$_x$As QW were studied by simultaneous Rutherford backscattering spectrometry (RBS) and particle induced x-ray emission (PIXE) measurements using a 1.95MeV $^4$He$^+$ 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$_x$As lattice were determined by directly comparing the angular scans about the $<110>$ and $<111>$ axial channels of the Mn K$_\alpha$ x-ray signals (PIXE) with those of the RBS signals of GaAs from the Ga$_{1-x}$Mn$_x$As QW. Due to the small total Mn content in all of the samples ($<8 \times 10^{14}$ 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 heterostructures 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$_x$As 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 ($\chi_{GaAs}$) and for the PIXE Mn x-ray signals ($\chi_{Mn}$) 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 $\chi_{Mn}$ for both samples follows the $\chi_{GaAs}$ 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 $\chi_{Mn}$ 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 $\chi_{Mn}$ 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$_x$As 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 $\chi_{Mn}$ in the <110> scan for the I-MDH indicates that
the concentration of Mn$_{\text{i}}$ is higher in the Ga$_{1-x}$Mn$_x$As 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 $\sim$1.5-2.0 [4], we estimate the fractions of Mn$_{\text{i}}$ to be $\sim$20% for I-MDH and $\sim$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$_x$As 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$_x$As 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 during the growth, resulting in degradation of ferromagnetism in Ga$_{1-x}$Mn$_x$As. The case of I-MDH thus resembles the instance of previously studied Ga$_{1-x}$Mn$_x$As layers doped with Be acceptors [12], where it was shown that in Ga$_{1-x}$Mn$_x$As 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$_x$As-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$_y$As/Ga$_{1-x}$Mn$_x$As/Ga$_{1-y}$Al$_y$As heterostructures the ratio of the Mn$_l$ donors to Mn$_{Ga}$ acceptors depends on the growth sequence of the Ga$_{1-x}$Mn$_x$As quantum well and the Be-doped Ga$_{1-y}$Al$_y$As barrier. The Fermi-level-induced reduction of the formation energy of Mn$_l$ 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
REFERENCES


FIGURE CAPTION

Fig. 1  Temperature dependence of normalized magnetization obtained from the Arrott plot analysis of the anomalous Hall effect data in three Ga$_{0.76}$Al$_{0.24}$As/Ga$_x$Mn$_y$As/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$_x$As QW for both I-MDH and N-MDH as a function of the incident tilt angles about the <110> and <111> axes (angular scans).
Fig. 1
Fig. 2