Enhancement of Curie temperature in Ga$_{1-x}$Mn$_x$As epilayers grown on cross-hatched In$_y$Ga$_{1-y}$As buffer layers

O. Maksimov, B.L. Sheu, G. Xiang, N. Keim, P. Schiffer, N. Samarth*

*Corresponding author. Tel.: +1-8148630136; fax: +1-2534848667.
E-mail address: nsamarth@psu.edu (N. Samarth).

Abstract

Relaxed In$_y$Ga$_{1-y}$As epilayers grown on (001) GaAs are known to exhibit a cross-hatched surface with ridges running along the [110] and [110] directions. We find that Ga$_{1-x}$Mn$_x$As epilayers grown on such buffer layers can have as-grown Curie temperatures ($T_C$) that are higher than the as-grown 110 K value typical of Ga$_{1-x}$Mn$_x$As/GaAs heterostructures. Further, low-temperature annealing leads to only modest additional increases in $T_C$; contrasting with the behavior in Ga$_{1-x}$Mn$_x$As/GaAs where $T_C$ typically increases significantly upon annealing. Our observations suggest that the initial concentration of Mn interstitials in as-grown Ga$_{1-x}$Mn$_x$As/In$_y$Ga$_{1-y}$As heterostructures is smaller than that in as-grown Ga$_{1-x}$Mn$_x$As/GaAs heterostructures. We propose that strain-dependent diffusion may drive Mn interstitials from the bulk of the growing crystal to more benign locations on the ridged surface, providing a possible route towards defect-engineering in these materials.

There is wide interest in the diluted magnetic semiconductor Ga$_{1-x}$Mn$_x$As for exploring proof-of-concept applications in semiconductor spintronics [1]. Ga$_{1-x}$Mn$_x$As is grown by low-temperature molecular beam epitaxy (LT-MBE), usually on GaAs (100) substrates, and exhibits ferromagnetism for 0.02 < $x$ < 0.09 with the ferromagnetic transition temperature ($T_C$) ranging up to ∼110 K for as-grown samples. Post-growth annealing at low temperatures (180°C < $T_{\text{anneal}}$ < 260°C) can increase $T_C$ up to ∼160 K [2–4]. The enhancement of $T_C$ is attributed to the migration of Mn interstitials (Mn$_i$) from the bulk of the sample to the surface; this reduces the compensation of exchange-mediating holes by these interstitial defects and hence increases $T_C$ [5,6]. This hypothesis is also supported by scanning tunneling microscopy of the Ga$_{1-x}$Mn$_x$As surface [7] and
by the capping-induced suppression of the annealing effect [8]. A number of attempts have been made to enhance \( T_C \) by combining the low-temperature annealing process with specific sample design such as Be modulation doping [9], N doping [10], or growth of Mn \( \delta \)-doped GaAs layers [11]. Here, we explore a promising alternate route toward the control of Mn\(_{1}\) defects in Ga\(_{1-\chi}\)Mn\(_{\chi}\)As. By carrying out epitaxial growth on strain-relaxed In\(_{0.12}\)Ga\(_{0.88}\)As templates with a rippled surface morphology. This appears to inhibit the formation of Mn\(_{1}\) defects in the bulk of the crystal during epitaxy, suggesting that a combination of inhomogeneous strain fields and misfit dislocation networks may provide a means of gettering Mn\(_{1}\) interstitials to benign locations. Our results suggest that it may be profitable to explore approaches to defect-engineering in these ferromagnetic semiconductors in a manner akin to that exploited in more standard semiconductors [12,13].

We focus on Ga\(_{1-\chi}\)Mn\(_{\chi}\)As epilayers grown by LT-MBE on a relaxed In\(_{0.12}\)Ga\(_{0.88}\)As buffer layer that is itself deposited on (100) GaAs. The lattice mismatch between the relaxed In\(_{0.12}\)Ga\(_{0.88}\)As buffer layer and GaAs (\( \Delta a/a_o \)) is \( \sim 0.9\% \). Hence, the Ga\(_{1-\chi}\)Mn\(_{\chi}\)As epilayers deposited on top of such a buffer layer are subject to a significant in-plane tensile strain compared to those grown on GaAs. Although earlier work has studied the influence of such “strain-engineering” on the magnetic anisotropy of Ga\(_{1-\chi}\)Mn\(_{\chi}\)As [14], we are unaware of any attempts to understand the influence of annealing on such samples. We demonstrate that the Curie temperature of as-grown Ga\(_{1-\chi}\)Mn\(_{\chi}\)As epilayers on In\(_{0.12}\)Ga\(_{0.88}\)As can be consistently higher than in samples grown on GaAs, with \( 105 \text{ K} < T_C < 125 \text{ K} \). Furthermore, in as-grown samples with such high values of \( T_C \), the ordering temperature only shows a modest increase upon annealing (reaching between 125 and 145 K). This behavior suggests that as-grown epilayers of Ga\(_{1-\chi}\)Mn\(_{\chi}\)As grown on In\(_{0.12}\)Ga\(_{0.88}\)As have a smaller fraction of Mn\(_{1}\) defects than epilayers grown on GaAs. Atomic force microscopy studies of our samples show a cross-hatched (CH) pattern with ridges running along [1 1 0] and [1 ˚ 1 0] directions. This observation suggests that strain-driven segregation of Mn\(_{1}\) towards the ridges and/or dislocations occurs during the MBE growth.

Samples are grown on epi-ready semi-insulating (Fe-doped) GaAs (100) substrates bonded with indium to Mo blocks. The growth is performed in an applied EPI 930 MBE system equipped with In, Ga, Mn and As effusion cells. The substrates are deoxidized using standard protocol, by heating to \( \sim 580\text{°C} \) with an As flux impinging on the surface. A thick (100 nm) GaAs buffer layer is first grown after the deoxidization. The samples are then cooled to \( \sim 500\text{°C} \) for the growth of a 750 nm In\(_{0.12}\)Ga\(_{0.88}\)As buffer layer. Following this, the growth is interrupted, the substrate temperature is decreased to \( \sim 250\text{°C} \), and a Ga\(_{1-\chi}\)Mn\(_{\chi}\)As epilayer is deposited. The growth is performed under the group \( V \) rich conditions with a As:Ga beam equivalent pressure ratio of \( \sim 12:1 \). The growth rate is \( \sim 300 \text{ nm/h} \) and the Mo block is rotated at a rate of 12 rpm for compositional uniformity. The growth mode and surface reconstruction are monitored in situ by reflection high-energy electron diffraction (RHEED) at 12 keV. The RHEED pattern shows a \( (1 \times 2) \) reconstruction during the Ga\(_{1-\chi}\)Mn\(_{\chi}\)As growth and there is no obvious indication of large-scale second phase formation (e.g. hexagonal MnAs precipitates). After removal from the MBE chamber, we anneal pieces cleaved out of each wafer at 250°C for 2 h in a high purity nitrogen gas (99.999%) flowing at a rate of 1.5 ft\(^3\)/h.

The Ga\(_{1-\chi}\)Mn\(_{\chi}\)As composition is measured by electron probe microanalysis; the thickness (estimated from RHEED oscillation measurements) is verified by cross-sectional scanning electron microscopy. Surface morphology is investigated using a tapping mode AFM. Structural properties are determined using X-ray diffraction. Magnetic properties are measured using a Quantum Design superconducting quantum interference device (SQUID) magnetometer.

Fig. 1A shows a \( \theta - 2\theta \) scan for a symmetric (0 0 4) reflection from a thick Ga\(_{0.94}\)Mn\(_{0.06}\)As epilayer on a GaAs buffer. The lattice mismatch between the Ga\(_{0.94}\)Mn\(_{0.06}\)As and GaAs is \( \Delta \alpha/\alpha_o \sim 0.52\% \), similar to the data reported by other groups [15]. Fig. 1B shows a (0 0 4) reflection from a thick Ga\(_{0.94}\)Mn\(_{0.06}\)As epilayer on a relaxed
**In0.12Ga0.88As buffer layer.** The lattice mismatch between the In0.12Ga0.88As and GaAs is $\Delta a/a_o \sim 0.89\%$. Since the lattice constant of In0.12-Ga0.88As is larger than that of Ga0.94Mn0.06As, the latter is under in-plane tensile strain and the position of the Ga0.94Mn0.06As peak shifts toward a larger angle (seen as a shoulder on the substrate peak). We note that the In0.12Ga0.88As buffer layer relaxes by the formation of dislocations. Since the Ga1–xMn_xAs films are grown directly on this InGa1–yAs without additional buffer layers, we expect that the misfit dislocations do not terminate at the interface and propagate throughout the Ga1–xMn_xAs. X-ray diffraction measurements indicate that the Ga1–xMn_xAs epilayers are coherently strained by the relaxed In0.12Ga0.88As buffer layer.

**Fig. 2** shows an AFM surface image of a Ga0.94Mn0.06As epilayer deposited on the In0.12-Ga0.88As buffer. The grown surface shows a CH pattern along the $[1 \bar{1} 0]$ and $[1 1 0]$ directions, with the ridges running along the former 2–3 times higher than those running along the latter; the spacing between the ridges is $\sim 1\mu m$. AFM measurements show that the CH pattern forms during the In$_y$Ga$_{1-y}$As growth, as reported in other studies of relaxed In$_y$Ga$_{1-y}$As epilayers grown on GaAs substrates [16]. The ridges are known to originate in the formation of misfit dislocations during the In$_y$Ga$_{1-y}$As growth [17] and the preferable striation along the $[1 \bar{1} 0]$ direction has been attributed to the anisotropy in surface diffusion length of In atoms [18]. We find that the ridges are the most pronounced for the thin Ga1–xMn_xAs epilayers and the surface becomes smoother for thicker epilayers. For example, the root mean square roughness decreases from 6.1 nm for a 30-nm thick Ga0.94Mn0.06As to 3.1 nm for a 240-nm thick Ga0.94Mn0.06As.

**Fig. 3** shows the SQUID magnetization data as a function of temperature for 30 nm thick Ga1–xMn_xAs epilayers grown on In1–yGa1–yAs (A, B) and GaAs (C) buffer layers. The $T_C$ of sample A (030716B) is not affected by annealing and stays at $\sim 125 K$, the $T_C$ of sample B (030716C) increases from 105 to 145 K, and the $T_C$ of sample C (030623A) increases from 86 to 138 K. Table 1 summarizes the values of $T_C$ for a set of samples grown under similar conditions. For Ga1–xMn_xAs grown on In1–yGa1–yAs, we routinely obtain as-grown $T_C$ in the range 105–125 K, and annealing boosts this up to the

---

**Fig. 1.** $\theta$–20 scans for the symmetric (004) Bragg reflections from Ga0.94Mn0.06As epilayers grown on GaAs (A) and In0.12Ga0.88As (B) buffer layers.
range 125–145 K. We find that for samples of Ga$_{1-x}$Mn$_x$As grown on GaAs during the same time frame, the $T_C$ is lower ($\sim 80$ K), while the annealing effect is far more pronounced, enhancing $T_C$ by as much as 70%. The statistical validity of this statement may be generalized by examining data published by several groups, clearly showing that in as-grown samples of Ga$_{1-x}$Mn$_x$As on GaAs, $T_C$ never exceeds 110 K, and is typically below 100 K [2–6,19,20,21].

We caution that Table 1 shows significant variation in the $T_C$ for as-grown and annealed samples grown on In$_{1-x}$Ga$_{1-y}$As buffers under nominally identical conditions: specifically, although several samples show an as-grown $T_C > 110$ K with little annealing effect, other samples have an as-grown $T_C < 110$ K with a very pronounced annealing effect. We do not find any obvious correlations of the observed behavior with physical parameters such as strain, surface roughness or defect density which are roughly similar for all these samples. A plausible reason for the observed sample-to-sample variations is the imprecise control over the substrate temperature; this is a common problem in MBE systems such as ours that rely on a radiatively coupled thermo-couple located behind the sample-mounting block.

Towards the end of this paper, we speculate further about physical reasons for the sensitivity of the annealing effect to variations in the substrate temperature.

Fig. 3. Temperature dependence of the remnant magnetization measured with out-of-plane magnetic field of 50 G for two 30-nm thick Ga$_x$Mn$_{1-x}$As epilayers grown on an In$_{0.12}$Ga$_{0.88}$As buffer layer: (A) 030716B with both as-grown and annealed $T_C = 125$ K and (B) 030716C with as grown and annealed $T_C = 105$ and 145 K, respectively. (C) Shows similar data for a 30-nm thick Ga$_x$Mn$_{1-x}$As epilayer grown on GaAs (030623A) with as-grown and annealed $T_C = 86$ and 138 K, respectively. Open symbols correspond to the as-grown data; solid symbols correspond to the data after annealing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Buffer</th>
<th>Thickness (nm)</th>
<th>$T_C$ as-grown (K)</th>
<th>$T_C$ annealed (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>030320A</td>
<td>Ga$<em>{0.94}$Mn$</em>{0.06}$As</td>
<td>InGaAs</td>
<td>75</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>030619A</td>
<td>Ga$<em>{0.95}$Mn$</em>{0.05}$As</td>
<td>GaAs</td>
<td>25</td>
<td>87</td>
<td>123</td>
</tr>
<tr>
<td>030623A</td>
<td>Ga$<em>{0.95}$Mn$</em>{0.05}$As</td>
<td>GaAs</td>
<td>30</td>
<td>86</td>
<td>138</td>
</tr>
<tr>
<td>030623B</td>
<td>Ga$<em>{0.94}$Mn$</em>{0.06}$As</td>
<td>GaAs</td>
<td>30</td>
<td>77</td>
<td>112</td>
</tr>
<tr>
<td>030701A</td>
<td>Ga$<em>{0.95}$Mn$</em>{0.05}$As</td>
<td>InGaAs</td>
<td>20</td>
<td>110</td>
<td>112</td>
</tr>
<tr>
<td>030701B</td>
<td>Ga$<em>{0.95}$Mn$</em>{0.05}$As</td>
<td>InGaAs</td>
<td>40</td>
<td>120</td>
<td>132</td>
</tr>
<tr>
<td>030703A</td>
<td>Ga$<em>{0.95}$Mn$</em>{0.05}$As</td>
<td>InGaAs</td>
<td>30</td>
<td>112</td>
<td>135</td>
</tr>
<tr>
<td>030703B</td>
<td>Ga$<em>{0.95}$Mn$</em>{0.05}$As</td>
<td>InGaAs</td>
<td>30</td>
<td>100</td>
<td>135</td>
</tr>
<tr>
<td>030714B</td>
<td>Ga$<em>{0.95}$Mn$</em>{0.06}$As</td>
<td>GaAs</td>
<td>20</td>
<td>70</td>
<td>110</td>
</tr>
<tr>
<td>030716A</td>
<td>Ga$<em>{0.94}$Mn$</em>{0.06}$As</td>
<td>InGaAs</td>
<td>30</td>
<td>105</td>
<td>135</td>
</tr>
<tr>
<td>030716B</td>
<td>Ga$<em>{0.94}$Mn$</em>{0.06}$As</td>
<td>InGaAs</td>
<td>30</td>
<td>125</td>
<td>125</td>
</tr>
<tr>
<td>030716C</td>
<td>Ga$<em>{0.93}$Mn$</em>{0.07}$As</td>
<td>InGaAs</td>
<td>30</td>
<td>105</td>
<td>145</td>
</tr>
<tr>
<td>030718B</td>
<td>Ga$<em>{0.94}$Mn$</em>{0.06}$As</td>
<td>InGaAs</td>
<td>30</td>
<td>105</td>
<td>140</td>
</tr>
</tbody>
</table>
As we mentioned in the introductory paragraph, Mn\textsubscript{I} defects play a critical role in limiting $T_C$ in Ga\textsubscript{1-x}Mn\textsubscript{x}As by compensating holes. Low-temperature annealing of the Ga\textsubscript{1-x}Mn\textsubscript{x}As alloy increases $T_C$ through the removal of Mn\textsubscript{I} from the bulk of the crystal to the surface. The differences that we observe in the $T_C$ of Ga\textsubscript{1-x}Mn\textsubscript{x}As/GaAs and Ga\textsubscript{1-x}Mn\textsubscript{x}As/In\textsubscript{y}Ga\textsubscript{1-y}As samples suggest that in the latter case a smaller fraction of Mn\textsubscript{I} defects is formed in the bulk of the crystal during sample growth. While we do not have the necessary measurements to further substantiate the microscopic details, we propose two speculative scenarios that could account for our observations. It is known that the lattice strain is not uniform across the surface of relaxed In\textsubscript{y}Ga\textsubscript{1-y}As films: it is lower at the top of the ridges and higher in the valleys [16]. Thus, it may be energetically more favorable for the highly mobile Mn\textsubscript{I} defects to segregate to the top of the ridges in a manner similar to the accumulation of InAs islands on the top of the ridges [16] and the alignment of InAs quantum dots along the [1 1 0] directions [22]. Alternatively, Mn\textsubscript{I} defects may be gettered by the misfit dislocation network that straddles the surface ridges: for instance, it is known that the misfit dislocation density is highest in the trough regions of CH samples [23], providing energetically favorable locations for the interstitials.

This model also allows us to speculate about the origin of the inconsistencies in the annealing behavior of samples grown under nominally identical conditions. Variations in substrate temperature invariably influence both the surface mobility and the Mn solubility: the former decreases at lower substrate temperatures, inhibiting the effective gettering of Mn\textsubscript{I} defects, while the latter decreases at higher substrate temperatures, possibly enhancing the formation of Mn\textsubscript{II} defects. Both these effects can increase the concentration of interstitials if the substrate temperature is either above or below the optimal temperature range; as a consequence, non-optimal substrate temperature can result in a lower as-grown $T_C$ with a pronounced enhancement of $T_C$ after annealing.

In conclusion, we have grown Ga\textsubscript{1-x}Mn\textsubscript{x}As epilayers by LT-MBE on relaxed In\textsubscript{0.12}Ga\textsubscript{0.88}As buffer layers that have a cross-hatched surface morphology. While the $T_C$ of as-grown Ga\textsubscript{1-x}Mn\textsubscript{x}As/In\textsubscript{y}Ga\textsubscript{1-y}As samples is typically higher than that of Ga\textsubscript{1-x}Mn\textsubscript{x}As/GaAs samples, a smaller increase in $T_C$ is observed upon annealing. We propose that the segregation of Mn\textsubscript{I} defects occurs during the MBE growth because of the ridge morphology of the relaxed In\textsubscript{y}Ga\textsubscript{1-y}As buffer layer and is responsible for our observations. Our observations suggest possible pathways to the controlled defect-engineering of Mn interstitials in Ga\textsubscript{1-x}Mn\textsubscript{x}As.

We thank J. Van Vechten for motivating the experiments described in this manuscript. We are also grateful to Khalid Eid and Keh Chiang Ku for additional sample growth, and to M. S. Angelone for help with the XRD and EPMA measurements. Authors (O. M. G. X. and N. S.) were supported by ONR Grants N00014-99-1-0071 and N00014-02-10996, and DARPA/ONR N00014-99-1-1093. Authors (B.L.S and P.S) were supported by DARPA N00014-00-1-0591 and NSF DMR-0101318. N.K. also acknowledges the support of the Penn State Physics REU site DMR-0097769.

References