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Enhancement of Curie temperature in $Ga_{1-x}Mn_xAs$ epilayers grown on cross-hatched $In_yGa_{1-y}As$ buffer layers

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Abstract

Relaxed $In_yGa_{1-y}As$ epilayers grown on (0 0 1) GaAs are known to exhibit a cross-hatched surface with ridges running along the [1 1 0] and [1 $\bar{1}$ 0] directions. We find that $Ga_{1-x}Mn_xAs$ 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 $Ga_{1-x}Mn_xAs$/GaAs heterostructures. Further, low-temperature annealing leads to only modest additional increases in T_C, contrasting with the behavior in $Ga_{1-x}Mn_xAs$/GaAs where T_C typically increases significantly upon annealing. Our observations suggest that the initial concentration of Mn interstitials in as-grown $Ga_{1-x}Mn_xAs$ /$In_yGa_{1-y}As$ heterostructures is smaller than that in as-grown $Ga_{1-x}Mn_xAs$/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 $Ga_{1-x}Mn_xAs$ for exploring proof-of-concept applications in semiconductor spintronics [1]. $Ga_{1-x}Mn_xAs$ is grown by low-temperature molecular beam epitaxy (LT-MBE), usually on GaAs (1 0 0) substrates, and exhibits ferromagnetism for $0.02<x<0.09$ with the ferromagnetic transition temperature (T_C) ranging up to $\sim$110 K for *as-grown* samples. Post-growth annealing at low temperatures ($180^\circ C < T_{anneal} < 260^\circ C$) can increase T_C up to $\sim$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 $Ga_{1-x}Mn_xAs$ surface [7] and

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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 δ-doped GaAs layers [11]. Here, we explore a promising alternate route toward the control of Mn_I defects in $Ga_{1-x}Mn_xAs$ 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_I 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_I 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 $Ga_{1-x}Mn_xAs$ epilayers grown by LT-MBE on a relaxed $In_{0.12}Ga_{0.88}As$ buffer layer that is itself deposited on (1 0 0) 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 $Ga_{1-x}Mn_xAs$ 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 $Ga_{1-x}Mn_xAs$ [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 $Ga_{1-x}Mn_xAs$ epilayers on $In_yGa_{1-y}As$ can be consistently higher than in samples grown on GaAs, with $105\,K < T_C < 125\,K$. 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 $Ga_{1-x}Mn_xAs$ grown on $In_{0.12}Ga_{0.88}As$ have a smaller fraction of Mn_I 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 $\bar{1}$ 0] directions. This observation suggests that strain-driven segregation of Mn_I towards the ridges and/or dislocations occurs during the MBE growth.

Samples are grown on epi-ready semi-insulating (Fe-doped) GaAs (1 0 0) 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°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°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°C, and a $Ga_{1-x}Mn_xAs$ 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 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 (1×2) reconstruction during the $Ga_{1-x}Mn_xAs$ 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 $Ga_{1-x}Mn_xAs$ 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 $\Delta a/a_o$ $\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

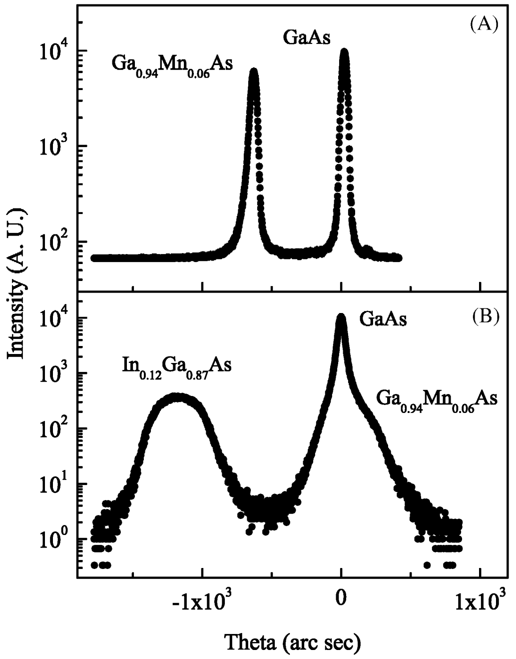

Fig. 1. $\theta-2\theta$ scans for the symmetric (0 0 4) Bragg reflections from $Ga_{0.94}Mn_{0.06}As$ epilayers grown on GaAs (A) and $In_{0.12}Ga_{0.88}As$ (B) buffer layers.

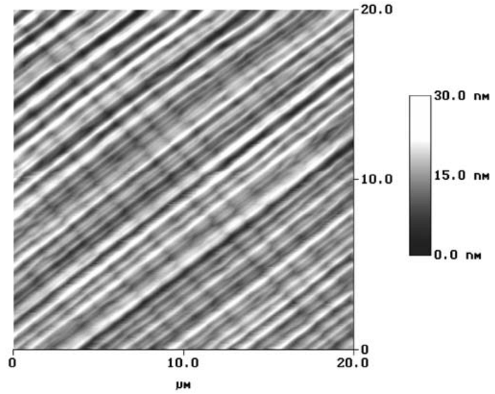

Fig. 2. An AFM surface image of a $Ga_{0.94}Mn_{0.06}As$ film grown on a $In_{0.12}Ga_{0.88}As$ buffer.

$In_{0.12}Ga_{0.88}As$ buffer layer. The lattice mismatch between the $In_{0.12}Ga_{0.88}As$ and GaAs is $\Delta a/a_o \sim 0.89\%$. Since the lattice constant of $In_{0.12}Ga_{0.88}As$ is larger than that of $Ga_{0.94}Mn_{0.06}As$, the latter is under in-plane tensile strain and the position of the $Ga_{0.94}Mn_{0.06}As$ peak shifts toward a larger angle (seen as a shoulder on the substrate peak). We note that the $In_{0.12}Ga_{0.88}As$ buffer layer relaxes by the formation of dislocations. Since the $Ga_{1-x}Mn_xAs$ films are grown directly on this $In_yGa_{1-y}As$ without additional buffer layers, we expect that the misfit dislocations do not terminate at the interface and propagate throughout the $Ga_{1-x}Mn_xAs$. X-ray diffraction measurements indicate that the $Ga_{1-x}Mn_xAs$ epilayers are coherently strained by the relaxed $In_{0.12}Ga_{0.88}As$ buffer layer.

Fig. 2 shows an AFM surface image of a $Ga_{0.94}Mn_{0.06}As$ epilayer deposited on the $In_{0.12}Ga_{0.88}As$ 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 $In_yGa_{1-y}As$ growth, as reported in other studies of relaxed $In_yGa_{1-y}As$ epilayers grown on GaAs substrates [16]. The ridges are known to originate in the formation of misfit dislocations during the $In_yGa_{1-y}As$ 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 $Ga_{1-x}Mn_xAs$ 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 $Ga_{0.94}Mn_{0.06}As$ to 3.1 nm for a 240-nm thick $Ga_{0.94}Mn_{0.06}As$.

Fig. 3 shows the SQUID magnetization data as a function of temperature for 30 nm thick $Ga_{1-x}Mn_xAs$ epilayers grown on $In_{1-y}Ga_{1-y}As$ (A, B) and GaAs (C) buffer layers. The T_C of sample A (030716B) is not affected by annealing and stays at ~ 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 $Ga_{1-x}Mn_xAs$ grown on $In_{1-y}Ga_{1-y}As$, we routinely obtain as-grown T_C in the range 105–125 K, and annealing boosts this up to the

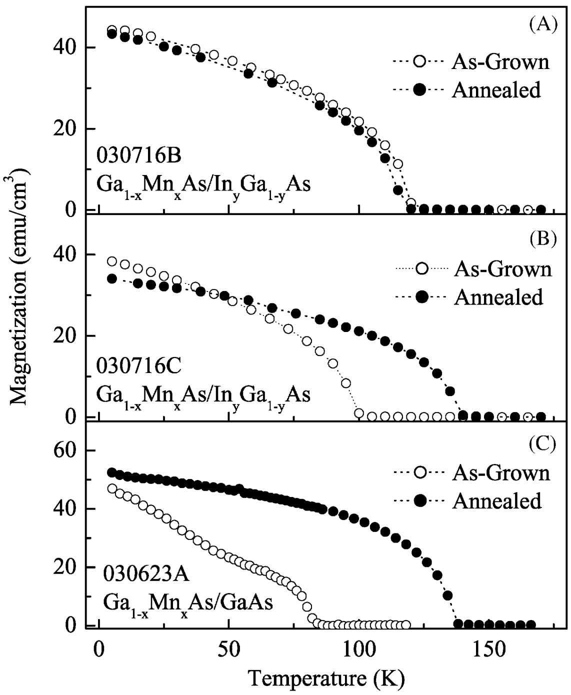

Fig. 3. Temperature dependence of the remnant magnetization measured with out-of-plane magnetic field of 50 G for two 30-nm thick $Ga_xMn_{1-x}As$ epilayers grown on an $In_{0.12}Ga_{0.88}As$ buffer layer: (A) 030716B with both as-grown and annealed $T_C = 125$ K and (B) 030716C with as grown and annealed $T_C = 105$ and 145 K, respectively. (C) Shows similar data for a 30-nm thick $Ga_xMn_{1-x}As$ 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.

range 125–145 K. We find that for samples of $Ga_{1-x}Mn_xAs$ 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 $Ga_{1-x}Mn_xAs$ 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 $In_{1-y}Ga_{1-y}As$ 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 thermocouple 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.

Table 1
Curie temperature for $Ga_{1-x}Mn_xAs$ epilayers of varying thickness grown on both $In_{0.12}Ga_{0.88}As$ buffer layers and GaAs buffer layers under nominally identical conditions

Sample	Composition	Buffer	Thickness (nm)	T_C as-grown (K)	T_C annealed (K)
030320A	$Ga_{0.94}Mn_{0.06}As$	InGaAs	75	120	120
030619A	$Ga_{0.95}Mn_{0.05}As$	GaAs	25	87	123
030623A	$Ga_{0.94}Mn_{0.06}As$	GaAs	30	86	138
030623B	$Ga_{0.94}Mn_{0.06}As$	GaAs	30	77	112
030701A	$Ga_{0.94}Mn_{0.06}As$	InGaAs	20	110	112
030701B	$Ga_{0.94}Mn_{0.06}As$	InGaAs	40	120	132
030703B	$Ga_{0.95}Mn_{0.05}As$	InGaAs	30	112	135
030703C	$Ga_{0.95}Mn_{0.05}As$	InGaAs	30	100	135
030714B	$Ga_{0.94}Mn_{0.06}As$	GaAs	20	70	110
030716A	$Ga_{0.94}Mn_{0.06}As$	InGaAs	30	105	135
030716B	$Ga_{0.94}Mn_{0.06}As$	InGaAs	30	125	125
030716C	$Ga_{0.93}Mn_{0.07}As$	InGaAs	30	105	145
030718B	$Ga_{0.94}Mn_{0.06}As$	InGaAs	30	105	140

As we mentioned in the introductory paragraph, Mn_I defects play a critical role in limiting T_C in $Ga_{1-x}Mn_xAs$ by compensating holes. Low-temperature annealing of the $Ga_{1-x}Mn_xAs$ alloy increases T_C through the removal of Mn_I from the bulk of the crystal to the surface. The differences that we observe in the T_C of $Ga_{1-x}Mn_xAs/GaAs$ and $Ga_{1-x}Mn_xAs/In_yGa_{1-y}As$ samples suggest that in the latter case a smaller fraction of Mn_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 $In_yGa_{1-y}As$ 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_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_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_I defects, while the latter decreases at higher substrate temperatures, possibly enhancing the formation of Mn_I 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 $Ga_{1-x}Mn_xAs$ epilayers by LT-MBE on relaxed $In_{0.12}Ga_{0.88}As$ buffer layers that have a cross-hatched surface morphology. While the T_C of as-grown $Ga_{1-x}Mn_xAs/In_yGa_{1-y}As$ samples is typically higher than that of $Ga_{1-x}Mn_xAs/GaAs$ samples, a smaller increase in T_C is observed upon annealing. We propose that the segregation of Mn_I defects occurs during the MBE growth because of the ridge morphology of the relaxed $In_yGa_{1-y}As$ buffer layer and is responsible for our observations. Our observations suggest possible pathways to the controlled defect-engineering of Mn interstitials in $Ga_{1-x}Mn_xAs$.

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References

[1] H. Ohno, in: D.D. Awschalom, D. Loss, N. Samarth (Eds.), Semiconductor Spintronics and Quantum Information, Springer, Berlin, 2002, pp. 1–30.
[2] K.W. Edmonds, K.Y. Wang, A.C. Neumann, N.R.S. Farley, B.L. Gallaher, C.T. Foxon, Appl. Phys. Lett. 81 (2002) 4991.
[3] K.C. Ku, S.J. Potashnik, R.F. Wang, S.H. Chun, P. Schiffer, N. Samarth, M.J. Seong, A. Mascarehnas, E. Johnston-Halperin, R.C. Myers, A.C. Gossard, D.D. Awschalom, Appl. Phys. Lett. 82 (2003) 2302.
[4] D. Chiba, K. Takamura, F. Matsukura, H. Ohno, Appl. Phys. Lett. 82 (2003) 3020.
[5] K.M. Yu, W. Walukiewicz, T. Woitowicz, I. Kiryliszyn, X. Liu, Y. Sasaki, J.K. Furdyna, Phys. Rev. B 65 (2002) 201303 (R).
[6] K.W. Edmonds, P. Boguslawski, K.Y. Wang, R.P. Campion, S.N. Novikov, N.R.S. Farley, B.L. Gallagher, C.T. Foxon, M. Sawicki, T. Dietl, M. Buongiorno Nardelli, J. Bernholc, Phys. Rev. Lett. 92 (2004) 037201.
[7] A. Mikkelsen, J. Gustafson, J. Sadowski, J.N. Andersen, J. Kanski, E. Lundgren, Appl. Surf. Sci. 222 (2004) 23.

[8] M.B. Stone, K.C. Ku, S.J. Potashnik, B.L. Sheu, N. Samarth, P. Schiffer, Appl. Phys. Lett. 83 (2003) 4568.
[9] T. Wojtowicz, W.L. Lim, X. Liu, M. Dobrowolska, J.K. Furdyna, K.M. Yu, W. Walukiewicz, I. Vurgaftman, J.R. Meyer, Appl. Phys. Lett. 82 (2003) 4220.
[10] R. Kling, A. Koder, W. Schoch, S. Frank, M. Oettinger, W. Limmer, R. Sauer, A. Waag, Solid State Commun. 124 (2002) 207.
[11] A.M. Nazmul, S. Sugahara, M. Tanaka, Phys. Rev. B 67 (2003) 241308 (R).
[12] A.S. Salih, H.J. Kim, R.F. Davis, G.A. Rozgonyi, Appl. Phys. Lett. 46 (1985) 419.
[13] E.R. Weber, D. Gilles, Proceedings of the Electrochemical Society, Vol. 90, 1990, pp. 585–600.
[14] H. Ohno, F. Matsukura, A. Shen, Y. Sugarawa, A. Oiwa, A. Endo, S. Katsumoto, Y. Iye, in: M. Scheffer, R. Zimmermann (Eds.), Proceedings of the 23rd International Conference on Physics of Semiconductors, World Scientific, Singapore, 1996, pp. 405–408.
[15] I. Kuryliszyn-Kudelska, J.Z. Domagala, T. Wojtowicz, X. Liu, E. Lusakowksa, W. Dobrowolski, J.K. Furdyna, J. Appl. Phys. 95 (2004) 603.
[16] Z.C. Zhang, Y.H. Chen, S.Y. Yang, F.Q. Zhang, B.S. Ma, B. Xu, Y.P. Zeng, Z.G. Wang, X.P. Zhang, Semicond. Sci. Technol. 18 (2003) 955.
[17] O. Yastrubchak, T. Wosinski, T. Figielski, E. Lusakowska, B. Pecz, A.L. Toth, Physica E 17 (2003) 561.
[18] K. Samonji, H. Yonezu, Y. Takagi, N. Oshima, J. Appl. Phys. 86 (1999) 1331.
[19] R.P. Campion, K.W. Edmonds, L.X. Zhao, K.Y. Wang, C.T. Foxon, B.L. Gallaher, C.R. Staddon, J. Crystal Growth 251 (2003) 311.
[20] T. Wojtowicz, W.L. Lim, X. Liu, Y. Sasaki, U. Bindley, M. Dobrowolska, J.K. Furdyna, K.M. Yu, W. Walukilewicz, J. Supercond. 16 (2003) 41.
[21] I. Kuryliszyn, T. Wojtowicz, X. Liu, J.K. Furdyna, W. Dobrowolski, J.M. Broto, O. Portugall, H. Rakoto, B. Raquet, J. Supercond. 16 (2003) 63.
[22] J. Siegert, S. Marcinkevicius, A. Gaarder, R. Leon, S. Chaparro, S.R. Johnson, Y. Sadofyev, Y.H. Zhang, Phys. Status. Solidi C 0 (2003) 1213.
[23] M. Albrecht, S. Christiansen, J. Michler, W. Dorsch, H.P. Strunk, P.O. Hansson, E. Bauser, Appl. Phys. Lett. 67 (1995) 1232.