Stoichiometric growth of high Curie temperature heavily-alloyed GaMnAs

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Heavily-alloyed, 100 nm Ga_{1-x}Mn_xAs (x>0.1) films are obtained via low-temperature molecular beam epitaxy utilizing a combinatorial technique which allows systematic control of excess arsenic during growth. Reproducible, optimized electronic, magnetic and structural properties are found in a narrow range of stoichiometric growth conditions. The Curie temperature of stoichiometric material is 150-165 K and independent of x within a large window of growth conditions while substitutional Mn content increases linearly, contradicting the prediction of the Zener Model of hole-mediated ferromagnetism.

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Greater understanding of defect formation is needed to further increase the Curie temperature ($T_C$) of ferromagnetic semiconductors, such as Ga$_{1-x}$Mn$_x$As, which hold promise for magneto-electronic devices. In typical molecular beam epitaxy (MBE) growth of GaMnAs, low substrate temperatures ($T_{sub}$) of $\approx 250$ °C are required to suppress precipitation of secondary crystal phases (e.g. MnAs) and incorporate a large fraction of Mn atoms as substitutional ($Mn_{Ga}$) acceptors in GaAs. Mn atoms also form double-donor interstitials ($Mn_i$) that compensate holes. Annealing films in air at temperatures of $\approx 180$ °C removes $Mn_i$, thus increasing the hole density ($p$) and $T_C$, in agreement with the Zener model of carrier-mediated ferromagnetism. This model also predicts that $T_C$ increases linearly with $x$, which is supported by studies over the last decade with $0.02 < x < 0.08$. More recently, MBE growth of GaMnAs with $x \geq 0.1$ was demonstrated in attempts to increase $T_C$. These films require reduced $T_{sub}$ ($\approx 180$ °C) and are limited to $\leq 10$ nm thickness; $T_C$’s after annealing reach the previous limit of $\approx 170$ K. In these studies, the effect of arsenic flux was not explored, though it should be a critical parameter at these conditions.

GaAs films grown at $T_{sub} \approx 250$ °C can contain double-donor arsenic antisites at concentrations $As_{Ga} \approx 10^{20}$ cm$^{-3}$ ($\approx 1\%$ of Ga sites). For a fixed $As:Ga$ flux ratio, $As_{Ga}$ in low-temperature (LT) GaAs increases exponentially as $T_{sub}$ is decreased below $\approx 300$ °C. Extended defects are prominent below 200 °C leading to polycrystalline films. Previously, we developed combinatorial (non-rotated) growth to continuously vary $As:Ga$ and, therefore, $As_{Ga}$, in GaMnAs films near the paramagnetic/ferromagnetic transition ($\approx 1\%$ Mn) with $T_{sub} = 250$ °C. There, excess arsenic flux of $\approx 1\%$ suppresses ferromagnetism, an unfeasible flux precision for rotated growths. Here we extend this technique to $T_{sub} \approx 150$ °C, where the metastable solubility limit of Mn in GaAs is increased beyond 10%. As in LT GaAs, increased
As$_{Ga}$ and extended defects occur unless As:Ga is precisely balanced to achieve stoichiometry. We discuss systematic variations of magneto-transport, ferromagnetism and crystal structure of GaMnAs ($x \geq 0.1$) as As:Ga is varied along the [110] direction (Fig. 1a inset). Optimal material is obtained in a narrow band of stoichiometric material. Stoichiometric, 100-nm thick films exhibit excellent crystalline quality and square magnetic hysteresis up to 165 K. Stoichiometric films grown with varying $x$ (>0.1), $T_{sub}$ and growth rate reach the same $T_C$ (150-170 K) after annealing; increasing $Mn_{Ga}$ does not increase $T_C$ as the Zener model predicts. We find the linear dependence of $T_C$ on $Mn_{Ga}$ is limited to $0.02 < x < 0.1$.

Samples are grown on 2”, semi-insulating (001) GaAs wafers by MBE as described in Ref. 13. The total fraction of Mn in the films ($x$) is calibrated from growth rate calibrations of MnAs and GaAs reflection high-energy electron diffraction (RHEED) intensity oscillations. After growth of the buffer layer, $T_{sub}$ is dropped to 150 °C and substrate rotation is stopped. Below 350 °C, the arsenic shutter is closed; it is opened for 10 s prior to LT growth to ensure an arsenic-terminated surface. $T_{sub}$ is measured in real-time during growth using band-edge thermometry with an accuracy of ±2 °C.\textsuperscript{15} During the first 5-15 nm of growth, $T_{sub}$ increases by ≈10 °C due to radiation from the heated Ga and Mn sources; $T_{sub}$ quickly stabilizes after heater power is dropped. We observe a 2D (streaky) $1 \times 2$ RHEED pattern on As-rich material transitioning to a 3D (spotty) pattern on Ga-rich material, observed by eye as mirror-finish (As-rich) transitioning to haze from Ga droplets on the surface.\textsuperscript{13} Wafers are cleaved into $\approx 3 \times 3$ mm$^2$ pieces along [110], yielding $\approx 17$ samples with systematically varying As:Ga.

Magnetometry and magneto-transport are measured on sample pairs with equal As:Ga (adjacent in the $[\overline{1}10]$ direction). Magneto-transport is measured in the van der Pauw geometry from 2-380 K with out-of-plane (hard axis) fields up to 14 T. $T_C$ is determined from
superconducting quantum interference device magnetometry (Quantum Design MPMS SQUID VSM) while warming in 50 Oe ([110] in-plane) after cooling from 350 K in 1 T. Saturation moment \( (M_{\text{sat}}) \) is determined from hysteresis loops (<0.5 T). We anneal sample pairs in air at \( \approx 180 \, ^\circ C \) until conductivity is maximized (Fig. 1c inset). High-resolution x-ray diffraction (HRXRD) is performed on half-wafers using a triple-axis (Phillips X’Pert MRD PRO) diffractometer with a 0.25° aperture for \( \approx 1 \, \text{mm} \) resolution along [110]. Lattice constant \( (a_{\text{GaMnAs}}) \) is determined from (004) \( \omega-2\theta \) scans.

Electronic, magnetic, and structural properties all depend critically on \( \text{As:Ga} \). Figure 1 plots data from a single 100-nm thick Ga\(_{0.84}\)Mn\(_{0.16}\)As film grown with \( T_{\text{sub}} = 150 \, ^\circ C \) at 0.852 Å/s. Room temperature longitudinal \( (\sigma_{xx}) \) and Hall \( (\sigma_{xy}) \) conductivity (Fig. 1a), \( T_C \) and \( M_{\text{sat}} \) at 5 K (Fig. 1b), and \( a_{\text{GaMnAs}} \) (Fig. 1c) all maximize at the same \( \text{As:Ga} \) where stoichiometry is achieved. \( \sigma_{xx} \) increases with annealing (Fig. 1c inset) due to out-diffusion of \( \text{Mn}_i \) from the bulk to the surface.\(^2\) Examples of \( \omega-2\theta \) scans in Fig. 1d reveal high-quality XRD epi-layer peaks with thickness fringes observed at stoichiometry (black points) which match dynamical simulations (line).\(^16\) The post-annealing epi-layer shift (red) shows a reduction of \( a_{\text{GaMnAs}} \) from removal of \( \text{Mn}_i \). This corroborates the model of Masek \textit{et al.}\(^{17}\) and results of Sadowski and Domagala\(^{18}\) demonstrating that the main contributor to \( a_{\text{GaMnAs}} \) expansion is \( \text{Mn}_i \). It follows that the largest number of \( \text{Mn}_i \) occur for stoichiometric material, the same \( \text{As:Ga} \) at which \( T_C, M_{\text{sat}}, \sigma_{xx}, \) and \( \sigma_{xy} \) are largest.

As-rich material displays a broad XRD peak without thickness fringes indicating low crystal quality (blue, Fig. 1d). At this \( \text{As:Ga} \), ferromagnetic MnAs particles (NiAs structure) are detected by magnetometry \( (T_C = 320 \, \text{K}) \). No remnant magnetization \( (M_{\text{rem}}) \) is observed at temperatures above the GaMnAs \( T_C \) in the stoichiometric region, but a \( M_{\text{rem}} \) of 0.1 \( \mu_B/\text{Mn} \) from
MnAs persists above the GaMnAs $T_C$ in the film with 35% excess arsenic. Excess arsenic might promote MnAs precipitation by creating extended defects that act as nucleation sites. MnAs is not observed in thinner As-rich films (7.5 nm), which could be below the critical thickness for defect formation. For our As-rich material, the same limits to $T_C$, $\sigma_{xx}$, and film thickness as in Refs. 5,6 are reproduced; these limits are overcome by achieving stoichiometry at precise $As:Ga$.

Excess arsenic and $M_{ni}$ significantly alter magnetic and electronic properties such as $T_C$, $M_{sat}$, coercive field ($H_C$), resistivity ($\rho_{xx}$) and magnetoresistance ($MR$). Figure 2a shows the $T_C$ increase to $\approx$165 K after minimizing defects, and we observe square hysteresis at this high $T_C$ (Fig 2b). Excess arsenic reduces the $H_C$ and $M_{sat}$ at 5 K (Fig. 2c). $\rho_{xx}$ and $MR$ increase by orders of magnitude at 10 K in samples with $M_{ni}$ and excess arsenic (Fig 2d). $M_{ni}$ increases $MR$ (at 14 T) from 3% to 44%, and excess arsenic ($As:Ga =12$) increases it to 87%. $\rho_{xy}$ switching occurs in all samples due to the anomalous Hall effect (Fig 2d).

The growth parameter space of heavily-alloyed GaMnAs is systematically explored with 16 non-rotated wafer growths with $0.1<x<0.22$, $120<T_{sub}<160$ °C, and growth rate varied from 0.198-1.41 Å/s. Figure 3a plots $T_C$ against $x$ for the stoichiometric samples from each heavily-alloyed wafer and also lightly-alloyed wafers ($x<0.1$, $200<T_{sub}<250$ °C). We observe the expected linear increase in $T_C$ with $x$ ($x<0.1$),\textsuperscript{3,4} but it does not extend to the heavily-alloyed regime, where $T_C = 150-165$ K post-annealing for all $x$ (maximum observed at $x=0.16$) despite the wide range of growth parameters. In contrast, $a_{GaMnAs}$ increases linearly up to $x\approx0.16$ for both as-grown and annealed films (Fig. 3b) and is fit using the model from Refs. 17,18. Assuming $As_{Ga}=0$ in the stoichiometric region, $a_{GaMnAs} = a_{GaAs} +0.02(x-z) +1.05z$, where $z$ is the atomic fraction of $Mn_{i}$ and $(x-z)$ is the atomic fraction of $Mn_{Ga}$. Linear fits, plotted as lines in Fig. 3b, demonstrate a constant fraction of interstitials ($z/x$) of 0.24 in as-grown samples and a reduction
of this fraction to 0.13 after annealing. The linear behavior indicates that $Mn_{Ga}$ and $Mn_i$ increase proportionally with $x$, up to $x \approx 0.16$. Contrary to the predictions of the Zener model, $T_C$ is independent of $x$ for $x > 0.1$ even though $Mn_i$ compensation maintains the same proportions in this heavily-alloyed regime.

In conclusion, heavily-alloyed, 100–nm thick GaMnAs films (0.1 < $x$ < 0.22) with reproducible, high magnetic ($T_C \approx 165$ K) and structural quality are grown utilizing a combinatorial technique to achieve stoichiometry. Magneto-transport, ferromagnetism, and lattice constant are critically dependent on $As:Ga$ for low $T_{sub}$, with stoichiometric, annealed material displaying optimal properties. While structural and magnetic data indicate a linear increase in $Mn_{Ga}$ up to $x \approx 0.16$, we do not observe the $T_C$ increase predicted in Ref. 3, suggesting the Zener model may not be applicable to the heavily-alloyed regime. Application of this combinatorial technique provides a reproducible method for obtaining high-$T_C$ GaMnAs and allows systematic exploration of the growth parameter space.

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Figure Captions

**Fig. 1.** Electrical, magnetic and structural dependence on As:Ga for a 100-nm thick Ga$_{0.84}$Mn$_{0.16}$As film grown without rotation. Inset: substrate and source geometry. (a) Room temperature longitudinal ($\sigma_{xx}$) and Hall ($\sigma_{xy}$) conductivity, (b) Curie temperature ($T_C$), saturation moment ($M_{sat}$) at 5 K and (c) lattice constant ($a_{GaMnAs}$) for different As:Ga. Stoichiometric region is shaded grey. Inset: $\sigma_{xx}$ versus anneal time, right axis is anneal temperature. (d) HRXRD scans along $\omega$-2$\theta$ near the (004) substrate peak measured on stoichiometric (as-grown and annealed) and As-rich samples labeled in the figure.

**Fig. 2.** Variation in ferromagnetism and magneto-transport due to stoichiometry and post-growth annealing (same film as Fig. 1). (a) Magnetic moment ($M$) and $\sigma_{xx}$ versus temperature ($T$). (b) $M$ versus magnetic field ($H$) hysteresis loops from the stoichiometric, annealed sample at various temperatures near $T_C$. (c) Hysteresis loops at 5 K. (d) Resistivity ($\rho_{xx}$) at 10K versus $H$. Magneto-resistance ($MR$) at 14 T is labeled in the figure. Hall resistivity ($\rho_{xy}$) versus $H$ for the annealed, stoichiometric sample.

**Fig. 3.** (a) $T_C$ versus $x$ for stoichiometric samples of Ga$_{1-x}$Mn$_x$As for 0$<x$<0.22 from many separate non-rotated growth runs. Data are shown both for as-grown and optimally annealed samples. Lines are guides to the eye. (b) Lattice constant ($a_{GaMnAs}$) versus $x$ from HRXRD scans as shown in Fig 1d. Lines are fits as described in the text indicating a constant fraction of interstitials ($z/x$) labeled in the figure. Blue data are for increasingly As-rich material, along the arrow.
Figure 1
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Figure 2
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Mack et al. (2023) have investigated the effect of alloying on the magnetic properties of a-GaMnAs. They found that the Curie temperature, $T_c$, varies linearly with the concentration of Mn, $x$, for both stoichiometric and heavily-alloyed samples. The lightly-alloyed samples exhibit a linear increase in $T_c$ with $x$, while the heavily-alloyed samples maintain a constant $T_c$. The ratio of As to Ga, $z/x$, has a significant impact on the magnetic properties, with values of $z/x = 0.24$ and $z/x = 0.13$ showing distinct behaviors in the plot.

Figure 3
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