Antisite effect on ferromagnetism in (Ga,Mn)As

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We study the Curie temperature and hole density of (Ga,Mn)As while systematically varying the As antisite density. Hole compensation by As antisites limits the Curie temperature and can completely quench long-range ferromagnetic order in the low doping regime of 1-2% Mn. Samples are grown by molecular beam epitaxy without substrate rotation in order to smoothly vary the As to Ga flux ratio across a single wafer. This technique allows for a systematic study of the effect of As stoichiometry on the structural, electronic, and magnetic properties of (Ga,Mn)As. For concentrations less than 1.5% Mn, a strong deviation from \( T_C \propto p^{0.33} \) is observed. Our results emphasize that proper control of As-antisite compensation is critical for controlling the Curie temperatures in (Ga,Mn)As at the low doping limit.

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I. INTRODUCTION

In (Ga,Mn)As, currently the most studied dilute magnetic semiconductor (DMS), a long-range ferromagnetic interaction between dilute Mn\(^{2+}\) spins is mediated by valence band (or defect band) hole spins.\(^{1,2}\) Most experimental work in this system has focused on achieving maximal Curie temperatures (\( T_C \)'s) in a technological drive to bring ferromagnetism in (Ga,Mn)As to more practical temperatures.\(^3\) In this vein, it was determined that a crucial limiting parameter of the \( T_C \) of as-grown (Ga,Mn)As is the incorporation of hole compensating crystalline defects, which are unintentionally formed due to the low growth temperature (~250 °C) and low solubility of Mn in GaAs. One such defect, the Mn interstitial (Mn\(_i\)), is considered to be a double donor compensating two holes each.\(^4\) These defects have shown a surprisingly high diffusivity allowing for their removal by using post-growth annealing at relatively low temperatures (~200 °C) that drive them to the surface.\(^5\) Consequently, the three dimensional hole density (\( p \)) and \( T_C \) after annealing can be drastically increased.\(^6\) Another well-studied defect in low temperature (LT) grown GaAs is excess arsenic. For substrate temperatures less than 300 °C, excess arsenic is incorporated by occupying a Ga-site, called an antisite defect (As\(_{Ga}\)) which - like the Mn\(_i\) defect is also a double donor.\(^7\) The density of these defects can reach 10\(^{20}\) cm\(^{-3}\), ~1% of Ga-sites, which is the same order of magnitude as typical Mn doping levels.\(^8\) By post-growth annealing at temperatures above 500 °C, As\(_{Ga}\) can be removed by the formation of metallic As precipitates\(^9\) however at these temperatures Mn also precipitates out of the (Ga,Mn)As solid solution as MnAs nano-particles.\(^10\)

Most experimental work on (Ga,Mn)As has been aimed at maximizing the \( T_C \) by controlling the compensating defects in the high doping regime, i.e. Mn \( \sim \)5-9\%. Such studies mainly focus on the reduction of Mn\(_i\) defects through post-growth annealing while loosely treating the problem of As non-stoichiometry. As\(_{Ga}\) defects are usually ignored in the high doping regime since Mn\(_i\) defects are the main source of carrier compensation, and their removal has led to dramatic increases in \( p \) and \( T_C \).\(^3\) On the other hand, hole compensation due to As\(_{Ga}\) could be as large as 10\(^{20}\) cm\(^{-3}\), which would shift \( T_C \) in this Mn-doping range by up to 10 K.

In contrast, near the ferromagnetic threshold of ~1% Mn, compensation due to As\(_{Ga}\) could dramatically alter the \( T_C \)'s since here the defect and dopant densities are roughly equal. Additionally, the concentration of Mn necessary for the onset of ferromagnetism should be a strong function of carrier compensation since the ferromagnetism depends strongly on \( p \); in the low doping limit ferromagnetism is likely extrinsically limited by hole compensating defects. We also note that theoretical work predicts a change in the mechanism of ferromagnetism in the low doping limit, near the insulator-metal transition,\(^11,12\) compared with the metallic limit at which \( T_C \propto p^{0.33} \) as predicted by the Zener-model.\(^3\)

The effect of excess As on the lattice constant of (Ga,Mn)As was treated by Schott et al.\(^13\) who used a different As-flux than another study\(^14\) and noted a change in the extrapolated lattice constant of zinc blende MnAs due to As\(_{Ga}\) incorporation. They followed-up their study by using 2 different As:Ga beam flux ratios, differing by 500% and noted large changes in the lattice constant of (Ga,Mn)As over a broad range of Mn-doping and substrate temperatures.\(^15\) These results were elaborated upon by Sadowski and Domagala, who measured lattice constant variation in Ga\(_{0.96}\)Mn\(_{0.04}\)As grown using 3 different As:Ga flux ratios and noted an interplay between Mn and As\(_{Ga}\) incorporation for this Mn doping regime.\(^16\) Campion et al. reported an improvement in structural and magnetic properties of (Ga,Mn)As films grown using As\(_2\) instead of As\(_3\).\(^17\) Their paper, however, does not describe the fluxes used for each As-species nor how the effective III-V ratio varies between these cases.
The same group has reported impressively high $T_C$'s over a broad range of Mn-doping levels, mentioning the importance of minimizing the As:Ga flux ratio although no data on the variation of this parameter were provided.\textsuperscript{21} Avrutin et al. carried out the first study that measured both the structural, electrical, and magnetic properties of (Ga,Mn)As using 2 different As:Ga flux ratios.\textsuperscript{18} They noted an optimization of the hole density, conductivity, and $T_C$ for the low As:Ga flux ratio, where fewer $A_{SGa}$ should be incorporated.

In this paper, we present the first systematic investigation of the effect of $A_{SGa}$ incorporation on the structural, electronic, and magnetic properties of (Ga,Mn)As in the low Mn-doping regime. The As:Ga flux ratio is smoothly varied within individual samples by using molecular beam epitaxy (MBE) without substrate rotation. The geometry of the MBE chamber inherently provides a gradient in the As:Ga flux ratio across the substrate of ±50%, while maintaining a roughly uniform Mn flux. In order to avoid formation of Mn and to achieve a high sensitivity to carrier compensation, we chose Mn doping concentrations of 1 - 2%, in the region of the onset of ferromagnetism. At Mn concentrations less than 1.5%, Mn has a larger formation energy than $A_{SGa}$. Thus, no interstitial Mn will form and all hole compensation should originate from $A_{SGa}$. Film morphology is measured in-situ by reflection high-energy electron diffraction (RHEED) and ex-situ by atomic force microscopy (AFM). Out-of-plane epitaxial strain is measured by high-resolution x-ray diffraction (HRXRD). Electronic properties at room temperature are measured by Hall effect in the Van der Pauw and Hall-bar geometries, and magnetic properties are measured by SQUID magnetometry (Quantum Design MPMS).

The epitaxial strain due to the incorporation of $A_{SGa}$ can be controlled by the As:Ga flux ratio, as previously reported.\textsuperscript{3,16,5} More interestingly, the electronic and magnetic properties reveal a strong sensitivity to $A_{SGa}$ compensation with conductivities and hole densities $p$ spanning over two orders of magnitude leading to a transition from paramagnetism to ferromagnetism for constant Mn densities (Sec. \textsuperscript{II} and \textsuperscript{IV}). Hole compensation due to $A_{SGa}$ reduces $p$ and therefore $T_C$. The As:Ga flux ratio is also observed to significantly alter film morphology (Sec. \textsuperscript{V}). In the As-rich condition, films attain maximum smoothness, show a high degree of $A_{SGa}$ related carrier compensation, and exhibit reduced or suppressed Curie temperatures. For As:Ga flux ratios at which the $p$ and therefore $T_C$ are maximized (stoichiometric condition, $A_{SGa} \sim 0$), the films remain two-dimensional (2D) but are rougher than the As-rich material. In the Ga-rich condition (small As:Ga flux ratios), films become three-dimensional (3D) with the accumulation of excess Ga on the surface leading to an order of magnitude increase in film roughness. At the minimum As:Ga flux ratio investigated, the roughest surfaces are observed with hemispherical Ga-droplets. The group-III enriched surface suppresses Mn incorporation during growth, leading to lower $p$ and $T_C$ values than in the As-rich condition.

In the low Mn-doped regime, where As-compensation limits hole density and ferromagnetic ordering, a strong deviation from the usual $T_C \propto \rho^{0.33}$ behavior is observed with $T_C \propto \rho^{0.09}$ for $x \leq 1.5\%$. Our results emphasize that proper control of hole compensation due to $A_{SGa}$ is critical to maximizing the value of $T_C$'s in the low Mn-doping regime. The combinatorial MBE growth approach used here could be applied to more complex LT grown GaAs-based heterostructures in which the As:Ga flux ratio is a strong control parameter.

II. MOLECULAR BEAM EPITAXY (MBE) GROWTH

All samples are grown on 2-inch diameter GaAs (001) substrates in a Varian Gen-II MBE system manufactured by Veeco Instruments, Inc. with a source to substrate distance of 5.4-inches. The substrate temperature is monitored by absorption band edge spectroscopy (ABES), which measures the substrate temperature in real-time through white-light transmission spectroscopy. The temperature stability during LT (Ga,Mn)As and GaAs growths is typically ±5°C. The growth rate of GaAs at the center of the wafer is 0.7 ML/sec as calibrated by RHEED intensity oscillations of the specular spot at 580°C. The Mn doping density is inferred from RHEED intensity oscillation measurements of the MnAs growth rate performed at 240°C. Measurements of the Mn density by secondary ion mass spectroscopy (SIMS) indicate that the RHEED calibration underestimates the density by up to 0.4% Mn, which provides a rough error estimate for the quoted Mn concentrations. We use $A_{S2}$ for all samples presented here, employing a valved cracker/sublimator. The beam equivalent pressure (BEP) of $A_{S2}$ and Ga are measured with a nude ion gauge at the center position of the substrate just prior to growth. The ratio of $A_{S2}$ and Ga BEPs, defined as $A_{S2}:Ga$, is proportional to the ratio of the atomic fluxes of As and Ga delivered to the growing surface. Unfortunately, a reliable quantitative conversion from BEP to atomic flux is difficult due to the uncertainties in the ionization efficiencies of each beam species.\textsuperscript{21} A rough estimate gives that the atomic flux ratio is 2.5 times smaller than the BEP ratios, where we assume that only $A_{S2}$ are present with a temperature equal to that of the cracking zone.

The following procedure is used for both non-rotated and rotated growths prior to deposition of the low temperature (LT) films. The wafer is first heated to 635°C with $A_{S2}:Ga \sim 35$ for oxide desorption, monitored by RHEED, and subsequently cooled to 585°C. While rotating at 10 RPM, a 300-nm GaAs buffer layer is grown using 5-s growth interrupts for every 15 nm of deposition resulting in a streaky $2 \times 4$ surface reconstruction RHEED pattern. While cooling the substrate to 250°C, the As-valve setting is reduced at 400°C for the desired
As : Ga value for LT growth. Prior to LT growth, a streaky 4 × 4 surface reconstruction is observed in the RHEED pattern. For rotated growths, once the substrate stabilizes at 250 °C the LT growth begins. For non-rotated growths, the substrate rotation is stopped at 400 °C and the wafer [110] crystal axis (perpendicular to the wafer major flat) is aligned along the As : Ga gradient direction (y-axis). This can be reproducibly accomplished noting the radial angle between the RHEED e-beam and substrate, fixed by the MBE chamber geometry, and finding a high symmetry crystal axis from the surface reconstruction pattern. All LT films are 100-nm thick at the center wafer position. After completion of the LT layer, they are cooled in a consistent manner to room temperature.

III. ROTATED (GA,MN)AS: CARRIER COMPENSATION AND QUENCHED FERROMAGNETISM

We first consider the case of rotated growth, examining the effect of Mn concentration and As : Ga on the electronic and magnetic properties. Four samples are grown with the same Mn concentration (2.3%), but with various As : Ga. Hole density data are from samples measured in the Van der Pauw geometry in a magnetic field up to 0.2 T. Figure 1a plots p and T_C of these samples as a function of As : Ga. Values of T_C are obtained from magnetization versus temperature scans as shown in Fig. 1b, selecting the point of maximum second derivative in M(T). The scans are performed during a field warm (50 Oe) after a field cool (1 T). The hole density decreases exponentially with the As : Ga, indicating that excess As in the form of AsGa donors are compensating MnGa acceptors. Correspondingly, T_C decreases with p, and for As : Ga ≥ 18 ferromagnetism is suppressed. This strong compensation effect is due to the fact that the AsGa donor and MnGa acceptor densities are similar in magnitude in this low Mn-doping regime, Mn < 2 %.

Using As : Ga = 10.3, for which the largest p and T_C are obtained (Fig. 1b), a series of four additional samples are grown with varying Mn concentration. For this series, variation in p and T_C occurs due to the varying concentration of MnGa, Fig. 1b. Clearly the hole density does not increase linearly with Mn concentration, which is indicative of a carrier compensation threshold. Based on this observation, a more careful optimization of As : Ga is necessary, as discussed in the next sections.

Figure 1c plots T_C as a function of p, summarizing data from Fig. 1a and b. We observe that varying the concentration of compensating AsGa donors (by varying As : Ga) has a qualitatively identical effect as varying the concentration of magnetic MnGa acceptors with respect to the carrier density and magnetic transition temperature. A fit of T_C ∝ p^{0.33} to the ferromagnetic samples in Fig. 1c: Mn doping ≥ 1.5%, reveals the usual functional dependence.

FIG. 1: Quenched ferromagnetism by As-compensation. Data from (Ga,Mn)As films grown at 250 °C using substrate rotation. (a) Samples were grown using a constant growth rate and Mn concentration but varying As : Ga. Room temperature hole density (p) is plotted on the left vertical axis as a function of As : Ga. (b) Similar data plotted for samples grown with a constant As : Ga. The corresponding Curie temperature (T_C) is plotted on the right vertical axis. (c) Data in (a) and (b) are replotted with T_C as a function of p. A fit to T_C ∝ p^{0.33} is shown for the ferromagnetic samples. (d) Magnetization versus temperature scans (field-warmed with B = 50 Oe) used to extract T_C shown in (b).
IV. NON-ROTATED (Ga,Mn)As: COMBINATORIAL VARIATION OF As : Ga

In order to systematically study the effect of the excess As on the electronic and magnetic properties of (Ga,Mn)As, we use a method of non-rotated growth in which the geometry of the MBE system provides a continuous variation in As : Ga across the wafer. Thus the advantage of a combinatorial approach is employed in which a single non-rotated growth provides the equivalent of twenty rotated growths of various As : Ga. The phase space of As : Ga and Mn concentration can be mapped-out in high-resolution while performing a much smaller number of growths than otherwise required.

Figure 2 schematically shows the position of the Ga Knudsen cell and the As valved-cracker/sublimator relative to the substrate position. The angle between the Ga and As$_2$ molecular beams provides a continuous variation in As : Ga across the y-axis of the substrate, as defined in the schematic. The variation of the As flux is measured by depositing a thick As film on a quartz wafer, covered by a shadow mask along the y-axis, with the substrate stabilized below room temperature. We have assumed that the deposition rate of As under these conditions is proportional to the As flux. A profilometer is used to measure the thickness of the As film along the y-axis. The normalized flux variation of As, plotted in Fig. 2a, is calculated by normalizing the thickness along y by the thickness at $y = 0$. The variation of the Ga-flux is measured using an optical measurement of a distributed Bragg reflector (DBR) and cavity structure grown in 2 separate steps. First, a 10 period GaAs/AlGaAs DBR is grown on a rotated 2-inch substrate in a larger, more uniform system (Veeco Gen III) with a source to substrate distance of 11-inches. This results in an extremely uniform DBR which is As-capped and transferred into the Gen II system. The As-cap is desorbed and a GaAs optical cavity layer is grown on the sample without substrate rotation. The reflectance spectrum of the sample is measured ex-situ at different points across the wafer and is fit to an optical model of the reflectance. Because the 10 period DBR was almost completely uniform, the thickness of the non-uniform GaAs layer grown in the Gen II could be accurately and unambiguously determined by fitting the measured optical spectrum to a computer model of the structure. Since the deposition is performed at 585˚C, the growth rate is independent of the As over-pressure, being limited by the group-III flux only. The normalized Ga rate, proportional to the Ga-flux, along the y-axis is plotted in Fig. 2a. Both the As and Ga flux variation are well fit by a second order polynomial (lines), which are used to convert y-axis position for non-rotated growths to As : Ga.

Next we consider the Mn flux variation across the substrate. Since the Mn Knudsen cell is roughly perpendicular to the y-axis, variation along this direction is expected to be small. In order to measure the Mn variation across the substrate, a 1-µm thick GaAs:Mn layer with Mn $\sim 4 \times 10^{17}$ cm$^{-3}$ is deposited at 400˚C with an As$_2$ over-pressure. At these conditions Mn incorporation is fully substitutional and excess As incorporation is negligible ($< 1 \times 10^{16}$ cm$^{-3}$), thus the hole density is proportional to the Mn:Ga flux ratio. The hole density variation across the $x$ and $y$ axes due to Mn:Ga variation is plotted in Fig. 2c and d, respectively. Along either axis, the
Mn:Ga ratio varies by 5–10%, which would correspond to variation in the Mn concentrations of 0.05 to 0.1%. As will be clear (Sec. VI), this variation in Mn concentration is negligible with respect to the As compensation effect under investigation.

V. FILM MORPHOLOGY AND STRAIN VERSUS \( \text{As:Ga} \)

To study the effect of \( \text{As:Ga} \) on the film morphology, the RMS roughness of non-rotated samples is measured across the y-axis by AFM. We describe results from two non-rotated films, without Mn doping and with 1.5% Mn. Both 5×5-\(\mu\)m\(^2\) and 1×1-\(\mu\)m\(^2\) area scans are measured every 3 to 4 nm along the y-axis of both wafers. The RMS roughness from these scans is plotted as a function of \( \text{As:Ga} \) (converted from y-position from Fig. 2b calibration) and representative AFM images of each region are shown in Fig. 3.

In the As-rich region from 11 < \( \text{As:Ga} \) < 14, AFM images reveal fully coalesced films with RMS roughness of 0.2 nm or less indicative of a 2D growth mode. RHEED observations of such films, from rotated growths at the same \( \text{As:Ga} \) condition, show sharp and streaky 2D reconstruction. In the As-rich to stoichiometric region from 9 < \( \text{As:Ga} \) < 11, films show a nanoscale-granular structure. For decreasing \( \text{As:Ga} \), this granular structure becomes more distinct and the film roughness increases, however it remains below 1 nm RMS. RHEED observations for films grown in this \( \text{As:Ga} \) range show a spotty reconstruction pattern indicative of a rough, but 2D surface, which we have found to be characteristic of films near the stoichiometric condition. In this region, the hole density of Mn-doped films reaches a maximum indicating the minimum of compensating As\(_{\text{Ga}}\) defects (Sec. VI).

Just below \( \text{As:Ga} \sim 9 \), the RMS film roughness increases by a factor of ten as \( \text{As:Ga} \) transitions from the stoichiometric condition to Ga-rich. AFM images of this region show the formation of 10-nm tall clover-shaped features 60-\(\mu\)m in diameter with a crater in the center. The RHEED pattern of these films shows additional spots indicative of 3D features on the surface. For \( \text{As:Ga} < 9 \), the surface roughness continues to increase with the appearance of larger droplet-like features. At the lowest \( \text{As:Ga} \) ratio, these hemispherical droplets are 50-\(\mu\)m tall and 240-\(\mu\)m in diameter. The large change in roughness across the non-rotated wafers is observable by eye under intense illumination, where the surface transitions from mirror finish at the As-rich region to a hazy surface in the Ga-rich region.

As observed in the roughness plot of Fig. 3 it appears that Mn-doping suppresses the onset of roughening toward smaller \( \text{As:Ga} \). In contrast, since Mn-doping increases the effective group-III flux, one would expect a shift in the onset of roughness to higher \( \text{As:Ga} \). This smoothing may be due to a surfactant effect of Mn on the surface. As discussed in Sec. VI the highest hole densities are observed in (Ga,Mn)As grown with \( \text{As:Ga} \) just before the transition from 2D to 3D surface, indicating that the growth kinetics at this stoichiometric condition do not significantly increase the density of hole compensating Mn\(_3\) donors.

HRXRD scans are obtained using a triple-axis (Phillips X’Pert MRD Pro) thin film diffractometer. We measure \( \omega-2\theta \) scans near the (004) Bragg peak of the (001)
FIG. 4: Film strain due to As non-stoichiometry and Mn incorporation in GaAs and (Ga,Mn)As non-rotated films measured by ω-2θ HRXRD scans near the (004) peak. (a)-(b) Data from a GaAs film at the As-rich wafer position (a) and stoichiometric position (b). Data (points) and dynamical simulations (lines) are plotted for various As:Ga densities. (c)-(d) Data from a (Ga,Mn)As film at the As-rich wafer position (c) and stoichiometric position (d). Data (points) and dynamical simulations (lines) are plotted using different Mn densities.

GaAs substrate. The diffraction patterns obtained for the non-rotated LT GaAs film at the position of highest As-compensation (As : Ga = 13 : 1) and at the stoichiometric condition (As : Ga = 9 : 1) are plotted in Fig. 4a and b, respectively. In the As-rich position, the epilayer peak appears as a shoulder at lower angle, reflecting the increase in the out-of-plane lattice constant, due to AsGa incorporation. We also note the thickness fringes indicative of the high quality of the film surface and interface. A dynamical HRXRD program is used to simulate the data assuming that the lattice constant of (Ga1−xAsx)As, a = 5.654 + 1.356xBest fit simulations in Fig. 4b give a film thickness 90 nm and AsGa = 4×10^{18} cm^{-3}. The additional fit with AsGa = 5×10^{19} cm^{-3} shows the error in the AsGa estimate is about 1×10^{19} cm^{-3}. The thickness of the epilayer is 10-15% thinner at the top edge than at the center of the wafer due to the smaller Ga-flux at this position, as shown in Fig. 2b. At the stoichiometric position the epilayer shoulder becomes small, only visible as a slight asymmetry on the left side of the substrate diffraction peak in Fig. 4b. Simulations using a film thickness of 100 nm yield AsGa = 4×10^{18} cm^{-3}, which is smaller than the uncertainty of the fits. A more precise estimate of the AsGa density is found from the hole density variation, discussed in Sec. VI. Thickness fringes disappear since the lattice constant of the epilayer is almost indistinguishable from that of the substrate.

Figure 4c and d plot the diffraction patterns from a non-rotated (Ga,Mn)As film with 1.5% Mn from the As-rich and stoichiometric positions, respectively. For these layers, strain due to Mn incorporation dominates the epilayer lattice constant obscuring the AsGa effect. Simulations are performed assuming that the lattice constant of (Ga1−xMnx)As, a = 5.654 + 0.476xMn The fits indicate a film thickness of 85 nm and 95 nm, and Mn concentration of 1.5% and 1.3% at the As-rich and stoichiometric positions, respectively. The variation in Mn concentration is not explained by the Mn:Ga ratio variation along y, Fig. 2b, which would predict a decrease in Mn concentration of up to 0.1%. The additional strain reduction may be due to the minimization of AsGa defects at the stoichiometric position, but the uncertainty of the HRXRD simulations prevents a more quantitative analysis.

VI. CARRIER DENSITY AND CURIE TEMPERATURE VERSUS As : Ga

A. Hole density gradient

Figure 5a and b show the variation in hole density for a series of non-rotated (Ga,Mn)As films of various Mn concentrations (a) along the y-axis, and (b) with y converted to As : Ga, using the Fig. 2b calibration. All the hole density data in the figures are from room temperature measurements of samples prepared in the Van der Pauw geometry (3×3 mm^2) in a magnetic field up to 0.2 T. Selective measurements of the hole density of patterned Hall-bars in magnetic fields up to 2 T agree with the Van der Pauw measurements to within 50%. Additional high field measurements at 7-9 T deviate from the low field data by up to 50 %.

The hole density varies by over two orders of magnitude across each wafer showing a maximum value near y ~ 6 mm corresponding to As : Ga ~ 9. The results are explained by a decreasing number of AsGa donors that compensate MnGa acceptors as As : Ga is reduced from the As-rich condition. The maximum of p along y corresponds to the position at which AsGa are minimized, the stoichiometric condition. A further reduction...
As:Ga ratio reported only two or three values of this parameter in increments of 200% or more.  

In the Ga-rich position (As:Ga < 9), the hole density decreases along with As:Ga, but remains constant as the Mn doping density is varied, Fig. 5a. This behavior is explained by a solubility limit for Mn, which is below any of the Mn doping levels used here. Decreasing As:Ga below the stoichiometric value leads to a Ga-rich surface that serves as a kinetic barrier for the incorporation of group-III substitutional dopants, such as Mn. One might consider the alternative possibility that interstitial incorporation of Mn might occur in these circumstances and could explain the reduction in hole density in the Ga-rich region. However, if Mn$_i$ donors were incorporating and compensating the Mn$_{Ga}$ acceptors, then the carrier density should change as the Mn-doping density is altered, which is not the case here. Preliminary SIMS data show a decreasing concentration of Mn in the Ga-rich region as the thickness increases, whereas the As-rich region reveals a relatively constant Mn depth profiles throughout the Mn-doped layer. In the Ga-rich region the Mn density can be $\sim 10^{20}$ cm$^{-3}$ lower than in the As-rich region.

The position of the hole density peak can be controlled by adjusting As:Ga at y = 0, which shifts the position of the stoichiometric condition along y. To demonstrate this, two wafers with identical Mn concentration of 1.5% are grown but with different As:Ga at y = 0. The variation of p along y is plotted in Fig. 5c. By increasing As:Ga at y = 0 from 8:1 to 9:1, the peak position (stoichiometric condition) is shifted by 1 cm toward the center of the wafer in a direction away from the As source. This shift is observable by eye as a change in the position of the transition region, where the surface changes from mirror finish to hazy. Converting the y-position to As:Ga.

Finally, we compare samples of equal Mn doping density grown with and without rotation. The hole densities of the rotated samples, Fig. 1b, match the hole densities for the non-rotated samples with similar Mn doping in the As-rich condition of As:Ga $\sim 10.5$, Fig. 5c. This indicates that the rotated sample set, presented in Fig. 1b, is grown under a slightly As-rich condition, on the right side of the hole density peak of Fig. 5c.

### B. Curie temperature gradient

The Curie temperature variation with As:Ga for two non-rotated (Ga,Mn)As films is plotted in Fig. 5a and b, together with the hole density variation. $T_C$ is determined from scans similar to those plotted in Fig. 1b. $T_C$ tracks the p variation with As:Ga, displaying a maxi-
As hole density peaks. In the As-rich portion of the wafer, minimum in Curie temperature in the same region where the hole density peaks. In the As-rich portion of the wafer, $\text{As}_\text{Ga}$ donors limit the hole density and therefore $T_C$. This effect is very clear, for example, with $\text{As} : \text{Ga} > 12$, where ferromagnetism is completely suppressed in both 1.5% and 1.25% samples due to hole compensation from $\text{As}$ non-stoichiometry in the form of $\text{As}_\text{Ga}$ donors.

The width and shape of the $T_C$ and hole density peaks are quite different. In general, the $T_C$ peaks are wider than the hole density peaks on the As-rich side, but are sharper than the hole density peak on the Ga-rich side of the wafer. To explain this behavior, we replotted data from several of the non-rotated (Ga,Mn)As wafers to examine the dependence of $T_C$ on the hole density. This dependence is plotted for the As-rich region ($\text{As} : \text{Ga} \geq 9$) in Fig. 6a, and for the Ga-rich region ($\text{As} : \text{Ga} \leq 9$) in Fig. 6b.

In the As-rich region, ferromagnetism is observed over a broad range in hole density from $10^{17}$ to $10^{19}$ cm$^{-3}$. For Ga-rich material, however, ferromagnetism is not observed over the same large range in hole densities where ferromagnetism is observed in the As-rich material, shaded grey. As described in Sec. V and VI A, hole density and film morphology measurements indicate that in the Ga-rich region Mn solubility is limited to well-below the level required for ferromagnetism, $< 0.5 \%$. This is probably due to the kinetic disadvantage of a group-III dopant on a heavily Ga-rich surface because of out-competition. The discrepancy in Fig. 6b between the Ga-rich region and As-rich region offers further support for this hypothesis. In this interpretation, Ga-rich conditions limit Mn$_\text{Ga}$ to low doping densities of less than $10^{19}$ cm$^{-3}$ ($< 0.05\%$ Mn). Whereas for similar hole densities in the As-rich material Mn$_\text{Ga} \sim 10^{20}$ cm$^{-3}$ ($\sim 1\%$ Mn). Thus ferromagnetism is possible in the As-rich material since there are sufficient Mn$_\text{Ga}$ acceptors, but the $T_C$ is limited by hole compensation due to As$_\text{Ga}$ donors. In the Ga-rich material, As$_\text{Ga}$ compensating donors are not present, but the Mn$_\text{Ga}$ density is well below the ferromagnetic limit.

The data in Fig. 6b for which $T_C \neq 0$ are fit to $T_C \propto p^{0.09}$ (line). This fit describes the data from two non-rotated wafers with Mn = 1.5% (Fig. 6b) and one wafer with 1.25% Mn over a large range in $p$ and $T_C$, over 13 data points. In the rotated growths presented in Fig. 6, $p^{0.33}$ behavior is observed for samples with $\geq 1.5\%$ Mn. There is no discrepancy between the non-rotated and rotated (Ga,Mn)As films if we conjecture that a change in the exponent from 0.33 to 0.09 occurs as the doping is reduced below 1.5% Mn. Since these doping levels are close to the ferromagnetic limit, a change in the dependence of ferromagnetism is not unexpected. The impurity band is fully merged with the valence band in the metallic region of high Mn-doping, where the $p^{1.33}$ is observed. But

FIG. 6: The Curie temperature gradient in non-rotated (Ga,Mn)As films due to As-compensation. The hole density ($p$) and $T_C$ are plotted as a function of As : Ga for two wafers with different Mn concentrations, (a) 1.25%, and (b) 1.50%. Lines guide the eye. The stoichiometric region is shaded grey, where excess As is minimized.

FIG. 7: Curie temperature ($T_C$) versus hole density ($p$) in several non-rotated (Ga,Mn)As films showing deviation from $p^{0.33}$. (a) Data are plotted from the As-rich region of the wafer ($\text{As} : \text{Ga} \geq 9$), and (b) from the Ga-rich region ($\text{As} : \text{Ga} \leq 9$). The shaded region marks $p$-values at which ferromagnetism is observed in As-rich material (a) and not in Ga-rich material (b). The line fit of data in (a) to $T_C \propto p^{0.09}$ is replotted in (b).
at low Mn-doping levels close to the insulating regime, the impurity band is separated from the valence band (Mott gap) where a disorder-based model of ferromagnetism is probably more accurate. Erwin and Petukhov predicted that a strong deviation from the metallic behavior of $T_C \propto p^{0.33}$ should occur in the low Mn-doping regime, $\sim 1.5\%$ Mn, with $T_C$ reaching a maximum in a partially compensated condition ($p$) and ferromagnetism disappearing for zero compensation (highest $p$); their model assumed that compensation was due to Mn$_i$ alone. This behavior is not clearly seen in our data, however the observed As$_{Ga}$ compensation was not treated in the model of Erwin and Petukhov.

VII. CONCLUSIONS

The electronic and magnetic properties of (Ga,Mn)As reveal a strong sensitivity to As$_{Ga}$ donors that compensate Mn$_{Ga}$ acceptors. By varying As : Ga, the hole densities of (Ga,Mn)As films are varied by more than two orders of magnitude, and, as a result, ferromagnetism can be enhanced or completely suppressed. For As-rich growth, films show the maximum smoothness, but lowest $p$ and $T_C$. If As : Ga is reduced, the film roughness increases up to the stoichiometric condition, where $p$ and $T_C$ are maximized. For Ga-rich growth, the film roughness increases by an order of magnitude as excess Ga accumulates on the surface. The group-III rich surface suppresses substitutional Mn incorporation leading to lower $p$ and $T_C$ values than in the As-rich condition. In the low Mn-doped regime, where As-compensation limits hole density and ferromagnetic ordering, a strong deviation from the usual $T_C \propto p^{0.33}$ behavior is observed with $T_C \propto p^{0.09}$ for $x < 1.5\%$. This dependence applies equally well to stoichiometric (Ga,Mn)As as it does to heavily As$_{Ga}$ compensated (Ga,Mn)As. This change in the hole density dependence of $T_C$ occurs in the doping region where the effects of a Mott gap and disorder are expected to alter the mechanism of ferromagnetism.

Our results emphasize that precise control of hole compensation due to As$_{Ga}$ is critical to maximizing the value of $T_C$’s in the low Mn-doping regime. The combinatorial MBE growth approach used here could be applied to more complex LT grown GaAs-based heterostructures in which As : Ga is a strong control parameter. The rapid and high-resolution mapping of growth parameter phase-space by this technique allows for systematic investigations not practicable using more traditional methods.

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