Structure and Magnetism in Ga-rich MnGa/GaN Thin Films and Unexpected Giant Perpendicular Anisotropy in the Ultra-Thin Film Limit

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Abstract

We report structural, surface, and magnetic investigations of ferromagnetic Ga-rich MnGa thin and ultra-thin films grown on semiconducting GaN(0001) using molecular beam epitaxy. The Mn:Ga composition ratio is varied from ≈ 1 (stoichiometric) to ≈ 0.42 (very Ga-rich) for different samples. We find that the L1₀ MnGa phase is preserved down to a Mn:Ga ratio of 0.81. As the Ga concentration increases, we observe the coexistence of more Ga-rich phases, namely Mn₃Ga₅ and Mn₂Ga₅. Room temperature scanning tunneling microscopy imaging reveals highly epitaxial films, with atomically smooth and highly reconstructed surfaces. Magnetic characterizations show how the magnetic properties evolve with changing composition and that giant perpendicular magnetic anisotropy is induced by reducing the size of our films.

Keywords: manganese gallium; gallium nitride, scanning tunneling microscopy; perpendicular magnetic anisotropy

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I. INTRODUCTION

Magnetic and spintronic nitride systems, free of rare earth elements and with sharp interfaces between constituent layers, are still at the heart of spin injectors and modern magnetic recording devices. Wide-gap semiconducting GaN is well known for its use in electronic and optoelectronic devices, and is therefore a great candidate for coupling with magnetic layers. Manganese gallium (MnGa) is a promising system for such coupling, since many of its phases are found to be ferromagnetic (FM) at room temperature for both Mn- and Ga-rich regimes.[1–4] In addition, the magnetic properties of MnGa are highly dependent on the Mn:Ga ratio present in the structure, as well as on substrate choice and thermal treatment.[2, 5–9]

The properties of Mn-rich MnGa thin films and nanostructures have been thoroughly investigated. Giant perpendicular magnetic anisotropy (PMA), high coercivity and spin polarization are some noteworthy properties that are of great interest in a large pool of applications.[10–16] Considering the less Mn-rich and stoichiometric (Mn:Ga=1) regimes, FM L1₀-structured MnGa(111) films have been studied in great detail. It was shown that these films are highly epitaxial when grown on GaN(0001); such sharp interfaces undoubtedly make MnGa/GaN a very attractive spintronic system.[17, 18] More recently, the surface structure of this system was investigated by means of experiment combined with theoretical calculations for growth under slightly Mn-rich conditions. It was found that under such conditions the Mn atoms incorporate at different rates: surfaces become highly Mn-rich, while the bulk retains a 1:1 stoichiometry; such behavior reveals a potential recipe for tuning, for example, magnetic properties by carefully controlling the surface reconstruction during growth.[19]

Despite the extensive literature on Mn-rich and stoichiometric MnGa alloys, the Ga-rich regime has received far less attention.[6, 20–23] In particular, the growth, structure, and magnetism of Ga-rich MnGa when deposited onto wide-gap GaN are still not addressed. From a technological point of view, in addition to having useful magnetic properties, an important requirement is to obtain epitaxial films with (atomically) smooth surfaces and sharp interfaces. Surface investigations of MnGa alloys in general or specifically MnGa/GaN, albeit important, are very sparse in the literature. The present work combines structural, surface, and magnetic studies of MnGa thin and ultra-thin films grown on GaN(0001) over

a range of Mn:Ga composition ratios that covers the Ga-rich regime. By exploring how the properties change as we cross the stoichiometric limit into the Ga-rich side, a more comprehensive understanding of this system can be achieved, ultimately adding useful information to a larger spectrum of Mn:Ga compositions.

II. EXPERIMENTS

The MnGa films are grown using molecular beam epitaxy (MBE) on freshly deposited GaN(0001) films on metal-organic chemical vapor deposition (MOCVD) grown GaN/Sapphire substrates (a more detailed growth procedure can be found in [19]). The sample temperature is held at $\approx 250^\circ\text{C}$ during MnGa deposition. The Mn:Ga composition ratios are varied from ≈ 1.00 (stoichiometric) to ≈ 0.42 (very Ga-rich), and we investigate thin (≈ 30 nm and ≈ 50 nm) and ultra-thin (≈ 3.3 nm and ≈ 7.8 nm) samples. The MnGa films are *not* annealed after growth.

After preparation, the samples are transferred *in-situ* to an adjacent ultra-high vacuum (UHV) analysis chamber, where room temperature scanning tunneling microscopy (STM) and Auger electron spectroscopy (AES) surface studies are performed. All STM images are obtained under constant current conditions. The AES spectra are acquired with an incident electron beam energy of 5 keV, and Mn:Ga AES ratios are calculated using peak-to-peak intensity ratios from derivative spectra corrected for sensitivity factors. The sensitivity factors for Mn, Ga, and N are specifically determined for our AES system using MBE-grown control samples.

Following removal from the vacuum chamber, structural and magnetic characterizations are performed. *Ex-situ* imaging is also performed using an atomic force microscope (AFM) operated in tapping mode. The orientation of the MnGa films is determined by X-ray diffraction (XRD) using a Rigaku MiniFlex II diffractometer with a Cu $K\alpha$ radiation source ($\lambda = 1.541$ Å).

Rutherford backscattering spectrometry (RBS) is carried out in order to determine the composition of the 30 nm and 50 nm thick samples. Experiments are performed using a 4.5-MV Tandem accelerator with 2.200-MeV and 3.035-MeV α beams. The samples are oriented at 75° with respect to the incident beam in order to get better depth profiles of the MnGa regions. The spectra are modeled using the Genplot/Rump software.

Magnetometry measurements are performed on the thin samples using a Lake Shore Cryotronics Model 7400 vibrating sample magnetometer (VSM). Hysteresis loops are recorded at room temperature in fields ranging from +16 kOe to -16 kOe for field directions both *in-plane* ($0^\circ \pm 0.5^\circ$) and *out-of-plane* ($90^\circ \pm 0.5^\circ$). All measurements provided here are taken with an averaging time per point of 10 seconds and a VSM moment sensitivity of 0.0042 emu. Magnetic characterization for the ultra-thin samples are performed using a Quantum Design superconducting quantum interference device (SQUID) magnetometer. We measure the magnetic hysteresis loops at room temperature in magnetic fields up to 30 kOe for both the *in-plane* and *out-of-plane* sample geometries. The diamagnetic contribution of the GaN substrate is subtracted from both VSM and SQUID loops.

III. RESULTS AND DISCUSSION

A. Structural results

Table 1 indicates the measured bulk (RBS) Mn:Ga ratios for the five thin MnGa films [no RBS measurements were performed on the ultra-thin samples, F and G, due to their small MnGa film thickness]. It can be seen that the Mn:Ga ratio varies from stoichiometric 1:1 (Sample A) to very Ga rich (sample E). Corresponding XRD scans are shown in Figure 1(a), with 2θ spanning 40° - 50° [we note that the scans were taken over a wider 2θ range, but we only show the region in which the main MnGa peaks appear].

Comparing the RBS and XRD measurements, we obtain very good agreement between bulk Mn:Ga ratios and the observed phases. For samples A and B, the main phases are identified as corresponding to $L1_0$ MnGa, as expected. As the Ga concentration increases (sample C), we observe the coexistence of $L1_0$ MnGa and more Ga-rich phases, namely Mn_3Ga_5 and Mn_2Ga_5 . Figure 1(b) shows the region in which MnGa(111) peaks appear for samples A, B, and C; as the Mn concentration increases a slight shift to the right is evident, in excellent agreement with previous observations by Bedoya-Pinto *et al.*[18] This shift is attributed to small changes in the d_{111} spacing as a result of changes in lattice parameter c . A plot showing the evolution of d_{111} spacing with sample stoichiometry is also shown in Fig. 1(b). We also find that the $L1_0$ phase is preserved down to a Mn:Ga ratio of 0.81, in agreement with previous reports.[15]

For samples D and E, the MnGa peaks disappear completely and only the two main Ga-rich phases are observed. For purely one phase samples containing either Mn_3Ga_5 (Mn:Ga $\approx$ 3:5) or Mn_2Ga_5 (Mn:Ga $\approx$ 2:5), we would expect to have Mn:Ga RBS ratios of $\approx$ 0.6 and $\approx$ 0.4, respectively. In turn, we measure slightly less than 0.6 for sample D - implying that we have some 2:5, and slightly more than 0.4 on sample E - agreeing again with the XRD data, which shows amounts of 3:5. Indeed, for alloys with a nominal composition $\text{Mn}_{37}\text{Ga}_{65}$, both Mn_3Ga_5 and Mn_2Ga_5 were found within the same crystal, although by further annealing only the stable Mn_3Ga_5 was preserved.[24] We note that the Mn:Ga composition ratio of $\text{Mn}_{37}\text{Ga}_{65}$, *i.e.* 0.587, is very close to our measured RBS Mn:Ga ratio of $\approx$ 0.58 for sample D.

Lattice parameters (a and c) and interplanar distances (d_{hkl}) for the observed phases and orientations are indicated in Table 2; we also report the lattice parameters for bulk samples.[3, 22, 23, 26] The three main phases observed in XRD are known to be tetragonal [3, 17, 22], although the peak at $\approx 46^\circ$ could also be identified as corresponding to the cubic MnGa_4 crystal. However, based on RBS and AES values (discussed below) it is more probable that this peak corresponds to Mn_2Ga_5 for our samples.

B. Surface studies

Referring back to Table 1, we can now compare the surface AES and bulk RBS Mn:Ga ratios. As it can be seen, the agreement is excellent for samples D and E, showing that these films are Ga-rich in both bulk and on the surface. Somewhat larger discrepancies are observed for samples A, B, and C; these differences can be explained by highly Mn-rich surfaces previously observed by STM on L1_0 -structured $\text{MnGa}(111)$ films deposited on $\text{GaN}(0001)$, where although the bulk of the film was stoichiometric, the surfaces presented mainly a Mn-rich 2×2 reconstruction.[19] This same reconstruction is observed (in varying amounts) on samples A, B, and C (see STM discussion below), thus giving rise to Mn:Ga AES ratios larger than RBS values.

For the case of ultra-thin sample F, AES measurements indicate that this sample is closest in surface composition to samples B and C (see Table 1). Indeed, STM investigations reveal similar structures on all of these samples. Figure 2(a) shows an STM image taken on sample F, where two main surface structures are visible. The featureless (lower) areas, when

better resolved, can be identified as the well-studied Mn-rich 2×2 surface reconstruction (see inset). On the top left corner (upper region) we observe row structures intersecting at $\approx 90^\circ$ and with varying periodicities. We note that the two structures from Fig. 2(a) have been previously observed by STM on similar samples.[19] A closer look at the row structure is shown in Fig. 2(b); it can be seen that the rows are separated by either $\approx 9.2 \text{ \AA}$ or $\approx 12.1 \text{ \AA}$. The rows are interrupted by grid- and double stripe-like patterns, emphasized by the square and rectangular boxes, respectively. While the 2×2 reconstruction seems to be independent of the film thickness, the row region becomes less complex as the thickness of the film increases. An STM image taken on sample B, and presented in the inset of Fig. 2(b), shows the evolution of this row structure with increasing film thickness. Atomic arrangements such as those indicated by the square and rectangular boxes in Fig. 2(b) are no longer visible; instead, structures having 3- and 4-row periodicities become dominant.

The exact surface Mn:Ga composition ratio for the row structure is unknown; it could be less Mn-rich than the 2×2 structure or it can even be very Ga-rich. In addition, the row and 2×2 structures can be found in varying amounts on the surface of a given sample, thus leading to different Mn:Ga surface ratios for samples A, B, C, and F. Being the most Mn-rich in bulk, using STM sample A is found to also exhibit the largest amount of 2×2 , consistent with higher AES ratios (see Table 1).

Considering now the more Ga-rich samples, when measuring the Mn:Ga AES ratio for sample G, a N peak is detected in addition to Ga and Mn peaks, an indication that the GaN layers are also probed. Therefore, a representative ratio for this sample is not easily measured, since the Ga peak is proportional to the total number of Ga atoms, from both MnGa and GaN surface layers (we note that this observation does not apply to sample F since N is not detected in the AES spectrum). However, the N peak can be explained by looking at Figure 3(a), which shows a $10\times 10 \mu\text{m}^2$ AFM scan of sample G. It can be seen that the growth is not uniform and results in the formation of 3D islands. These islands cover $\approx 46 \%$ of the surface and their heights are measured to be on average $\approx 17 \text{ nm}$; based on the measured coverage, this height corresponds to a uniform MnGa film of $\approx 7.8 \text{ nm}$, as given in Table 1. The Mn:Ga AES ratio reported in Table 1 for sample G is an estimate based on the contribution to the AES signal of only Ga atoms contained in the MnGa islands visible in the AFM scans. This way, we find that sample G is close in surface composition to sample D. In fact, this conclusion is also supported by comparing STM images taken on samples D

and G, from where we find similar surface structures (see STM results below). By looking at Fig. 3(b), which shows a $10 \times 10 \mu\text{m}^2$ AFM scan of sample D, it can be observed that as the thickness increases the sample morphology is preserved and the film becomes more uniform, with GaN layers no longer visible.

Upon investigating the surface of sample G with STM, two distinct and adjacent row structures are mainly observed and they are shown in Fig. 4(a) [presented in derivative mode]: (i) on the left (lower) terrace, a relatively uniform row structure can be seen; (ii) on the right (upper) terrace, a more complex row structure is visible, consisting of interrupted raised rows (some indicated by arrows) and small patches of more uniform arrangements (highlighted by the dashed box). The difference in height between the left and right regions varies between 1.6 nm and 2.3 nm, in agreement with AFM height measurements on a given island.

A 3D perspective view of the area shown in Fig. 4(a), with emphasis on the lower region, is presented in Fig. 4(b). The uniform row region shows a large modulation on the surface, with a wavelength of about 35 nm and a height of $\approx 1 \text{ \AA}$. This type of surface effect is unique to ultra-thin sample G and can be explained by composition and/or strain gradients within the structure.[27, 28] It is well known that the stability of the film surface can be influenced by the degree of lattice mismatch between the film and the substrate, leading, for example, to changes from layer-to-layer into 3D island growth; the film surface can also be influenced by stresses generated by compositional inhomogeneities. Some examples include the well-studied InGaN/GaN and SiGe/Si systems.[29–31] In these strained structures, the degree of relaxation was found to affect the incorporation rate of one of the species, thus inducing a composition strain effect. Undulations observed on the surface were attributed in some cases to transitions from a homogeneous lattice strain to a more periodic inhomogeneous lattice strain, caused by increasing the layer thickness.

Closer views of the two structures from Fig. 4(a) are shown in Figs. 4(c) and 4(d). A line profile taken along line path L1 in Fig. 4(c) shows that the rows are separated by $\approx 7.8 \text{ \AA}$, and that their corrugation heights differ by up to $0.4 \text{ \AA}$; along a given row, we measure the distance between two features to be $\approx 5 \text{ \AA}$. Fig. 4(d) shows a similar area to the one on the right in Fig. 4(a); taking a line profile along part of this image (line path L2) shows that in this case also, we have different corrugation heights (which can be as high as $0.65 \text{ \AA}$) between rows running parallel to each other. The surface shown in Fig. 4(d)

is complex, as indicated by the atomic arrangements enclosed by dashed boxes, which are different depending upon the distance separating the raised rows. In addition, measurements taken on the right terrace in Fig. 4(a) reveal relatively random raised-row spacings ranging between ≈ 11 Å and ≈ 68 Å.

Topographic STM images taken on sample D are shown in Figs. 5(a) and 5(b). Once again, a raised-row structure is observed, with spacings similar to the ones measured on the surface of Sample G [on the right terrace in Fig. 4(a)]. A more uniform structure can be seen in the center of Fig. 5(a), with spacings denoted as α and measured to be ≈ 17 Å (see inset). Some of the highest rows on the surface are found to be separated by multiples of α . Comparing Figs. 5(a) and 5(b), after performing drift correction, it can be observed that similar structures appear on the same sample, only rotated by $\approx 60^\circ$. Although all observed phases have an underlying tetragonal unit cell (two-fold symmetry), the formation of 60° -rotated domains takes place during growth, given the three-fold symmetry of the GaN substrate. In total, three different rotation orientations are seen, also visible in the AFM scans from Fig. 3. A similar behaviour was observed previously on the $L1_0$ -structured MnGa(111) thin films grown on GaN.[19]

It should be mentioned that the two surface structures that appeared for the more Mn-rich samples (Fig. 2) are not observed on the Ga-rich samples. This is consistent with XRD results, which do not show any $L1_0$ MnGa peaks for samples D and E.

Due to the complex surface reconstructions observed in STM, a match with a theoretical model for the proposed Ga-rich phases, Mn_3Ga_5 and Mn_2Ga_5 , is very challenging. As can be observed from XRD measurements the growth takes place along high-index planes for both crystals, which can result in very complex surface arrangements. Moreover, for the case of $L1_0$ -MnGa(111) it was shown theoretically and experimentally that not only the surfaces are reconstructed, but the surface density of states (DOS) is dominated by the Ga atoms.[19] In another study, investigating sub-monolayer amounts of Mn deposited on GaN(0001), the Mn atoms were found to dominate the surface DOS in the observed $\sqrt{3}\times\sqrt{3}$ -R30° MnGa structure.[25] Therefore, it is reasonable to assume that we have similar behaviour in the current study, with possibly Mn and/or Ga atoms dominating the surface of different structures, thus complicating the STM image interpretation. The STM surface structure identification is beyond the goal of the present work and could be the subject of a future study.

C. Magnetic properties

Figures 6(a) and 6(b) show VSM magnetization versus magnetic field loops measured on the thin samples, for magnetic fields oriented parallel and perpendicular to the sample surface. The magnetization values are normalized by the sample volume and parameters extracted from the VSM loops are reported in Table 3. Overall, all films exhibit magnetic anisotropy to some degree, as visible from the more square *in-plane* hysteresis loops. Also, we observe a gradual decrease in magnetization as the Ga-concentration increases.

Starting with the more Mn-rich samples (A, B, and C), it can be seen that the highest magnetization (371 emu/cm^3) is obtained for the stoichiometric (Mn:Ga=1) sample A. This value is consistent with previous published results for MnGa films of similar composition grown on GaN(0001) substrates.[9, 17, 18] Reports on $L1_0$ MnGa films deposited on GaAs as well as GaN substrates find that as the Mn content increases the lattice constant c decreases. Furthermore, with increasing Mn concentration, a decrease in magnetization, accompanied by an increase in coercivity, is observed. This behavior was explained by the induced strain in the MnGa lattice.[2, 18, 32] Although we observe a similar tendency for lattice constant c and consequently for the d_{111} spacing [see Fig. 1(b)], the trends in magnetization and coercivity are quite different and cannot be easily quantified. As the Ga concentration increases (or Mn concentration decreases), we observe a decrease in magnetization (down to 235 emu/cm^3 for sample C), although not a drastic change in coercivity. In fact, samples A and C have about the same coercive field (3.2 kOe), whereas sample B has the highest value (3.9 kOe). In addition to strain present in the lattice, our films are not purely one phase as determined by XRD. Therefore, we have to take into consideration the appearance of more Ga-rich phases and their effect on the magnetic properties. For example, by looking at Fig.6(a), small kinks in the (*in-plane*) M-H curves for samples A and B are visible, reflecting the interaction between different magnetic phases. The effects of strain and competing magnetic phases cannot be easily separated and can modify not only the magnetization and coercivity, but also the magnetic anisotropy.[2]

Compared to the more Mn-rich films, the M-H curves for samples D and E show smaller magnetization values along with decreased coercivity. A closer look at sample D reveals a stepped hysteresis loop. Both Mn_3Ga_5 and Mn_2Ga_5 (detected by XRD within this sample) are known to be FM and their magnetic interaction can result in magnetic loops of this

shape, as previously shown for Ga-rich MnGa films deposited onto NaCl substrates.[4, 20] For the most Ga-rich sample E, the loop is more uniform, in agreement with the sharp Mn_2Ga_5 peak (suggestive of mainly one phase) observed in XRD. Comparing samples D and E, we observe that as we increase the Ga-concentration, the magnetization decreases and the coercivity increases.

Magnetic anisotropy is known to be induced by depositing MnGa films on various substrates, as shown by Wang *et al.*[9]; the growth temperature and subsequent thermal treatment also play a role in the resulting magnetic properties.[2, 4] However, all of our films were deposited onto the same substrate, at the same temperature, and no annealing took place after growth. Therefore, the mechanism responsible for tailoring the magnetic properties for the thin films is the change in Mn:Ga ratio during growth.

Another way of tailoring the magnetic properties is by decreasing the thickness of our films. This is clear from the SQUID magnetometry data shown in Figs. 6(c) and 6(d) for ultra-thin samples F (more Mn-rich) and G (more Ga-rich). Compared to thicker films of similar composition (samples B and C), the coercivity of sample F drastically decreases for both orientations. For the parallel orientation of sample G, the coercivity (0.9 kOe) is comparable to that of sample D (0.8 kOe) and a similar stepped hysteresis loop is observed.

Unexpectedly, in addition to becoming soft ferromagnets ($H_c \approx 0.1$ kOe for the perpendicular direction), samples F and G exhibit giant PMA; in the parallel orientation not even fields as high as 30 kOe can saturate the samples, whereas fields as small as 9 kOe are enough to saturate the perpendicular direction. Magnetic parameters extracted from SQUID loops are reported in Table 3.

Even more unexpected are the giant saturation magnetization values for the perpendicularly magnetized films (≈ 1627 and ≈ 887 emu/cm³ for samples F and G, respectively). Considering an $L1_0$ structure for film F (based on the STM and AES results), we calculate the magnetic moment per Mn atom to be $4.84 \pm 0.52 \mu_B$, surprisingly large considering the fact that for thicker film B, the calculated moment is only $0.81 \pm 0.12 \mu_B$. Combined with the large PMA, it appears that (i) most of the Mn 5d-electrons contribute to the magnetization and (ii) they are almost fully magnetically aligned perpendicular to the film surface. The mechanism responsible for the increased moment is unclear; surface/interface anisotropy contributions combined with the very small thickness could be a possible cause. However, further investigations are necessary.

Although large PMA is observed in (Mn-rich) L1₀- and DO₂₂-structured thicker (≈ 100 nm) MnGa films, in general the coercivities are very large (≈ 5 -25 kOe) and the magnetization values are significantly lower (≈ 80 -280 emu/cm³). [11, 15, 16] It is interesting to note that our magnetization and coercivity values for the ultra-thin films are more quantitatively comparable to L1₀-structured FePt ($M_s \approx 1000$ -1250 emu/cm³ and $H_c \approx 1$ kOe) and CoPt ($M_s \approx 800$ emu/cm³ and $H_c \approx 0.2$ -1 kOe) thin and ultra-thin films prepared under various conditions. [33–36] This comparison is all the more remarkable considering the fact that FePt and CoPt systems are alloys comprised of transition metals, whereas the MnGa system is a Heusler-type alloy. The common denominator for these three systems is the fact that, under certain conditions, they crystallize in the L1₀ phase, which is responsible for some of their special magnetic properties. [34]

Although the thicker samples also exhibit anisotropy, it is mostly *in-plane* and not as pronounced as for the ultra-thin samples. For the case of film F, we find the anisotropy field H_a to be 248 ± 8 kOe. We also calculate the uniaxial magnetic anisotropy constant using $K_u = K_{eff} + 2\pi M_s^2$, where K_{eff} is the area between the *in-plane* and *out-of-plane* loops, and $2\pi M_s^2$ gives the shape anisotropy contribution. Thus we find that $K_u = 2.19 \pm 0.28 \times 10^8$ erg/cm³; this value is extremely large, about five to seven times larger than some L1₀-structured FePt and CoPt films, and about ten times larger than Mn_xGa films grown on GaAs substrates. [15, 34]

It appears that the giant PMA is induced somewhere between 50 nm and our respective thicknesses for samples F and G; further investigations can look into finding this transition point. We expect that if the observed anisotropy comes from a surface effect, then it should disappear quickly with increasing thickness, similar to the case of Co/Pt multilayers [37]; if the anisotropy comes from bulk, then it should persist to large thicknesses, just as FePt films. Furthermore, strain present in the ultra-thin films can also affect the anisotropy. Although strain could be responsible for the large PMA in film G (as already discussed, STM imaging reveals such effects), film F does not appear to exhibit strain effects. RHEED measurements on films F (≈ 3.3 nm) and B (≈ 50 nm) do not indicate any *in-plane* lattice constant differences between these two films, which is expected given the fact that L1₀ MnGa(111) grows with almost no lattice mismatch on GaN. [17] Therefore, there must be a different mechanism that is responsible for the large PMA in film F. Upon decreasing the sample thickness, interface and surface contributions to the magnetic anisotropy become

significant, leading, for example, to changes in the easy magnetization axis from *in-plane* to *out-of-plane*. A combination of all the above effects can play a role in the resulting film properties. Therefore, future work will also address detailed investigations of how the morphology, surface structure and magnetic properties change as a function of thickness, composition and thermal treatment.

IV. CONCLUSIONS

In summary, we combined various techniques to study the structural and magnetic properties of Ga-rich MnGa films deposited onto GaN(0001) substrates. Films with compositions ranging from stoichiometric to very Ga-rich and with thicknesses in the range 3.3 nm to 50 nm are investigated. Structurally, as we cross the stoichiometric limit into the Ga-rich regime, we observe that in addition to the expected L1₀ phase, more Ga-rich phases develop. Using scanning tunneling microscopy imaging at room temperature, we probe the surface structure and film quality. We find that all films have very smooth and highly reconstructed surfaces. Magnetic investigations show that all MnGa films exhibit ferromagnetism, even the ones pertaining to the very Ga-rich case. In addition, giant perpendicular magnetic anisotropy is observed as the thickness of the films is reduced to several nanometers, together with an unexpected increase in magnetic moment for the L1₀-structured ultra-thin film. Future studies will address possible changes in structure and magnetic properties induced by changing the thickness, deposition temperature, composition, or by applying post-growth annealing. We emphasize the importance of surface studies in determining the composition, thickness, and structure for the ultra-thin films, parameters that would be challenging to quantify otherwise.

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TABLE 1: MnGa film thickness, Mn:Ga RBS and Mn:Ga AES ratios. The values marked with * are estimated given the coverage observed in AFM (see text for details).

Sample	MnGa film thickness [nm]	Mn:Ga RBS ratio	Mn:Ga AES ratio
A	50.0 ± 2.0	1.00 ± 0.15	1.21 ± 0.24
B	50.0 ± 2.0	0.95 ± 0.10	1.02 ± 0.20
C	50.0 ± 2.0	0.81 ± 0.08	0.95 ± 0.19
D	50.0 ± 2.0	0.58 ± 0.06	0.61 ± 0.12
E	30.0 ± 1.0	0.42 ± 0.08	0.45 ± 0.09
F	3.3 ± 0.3	-	0.98 ± 0.19
G	$7.8 \pm 1.8^*$	-	$0.56 \pm 0.11^*$

TABLE 2: MnGa phases, lattice parameters and orientations as obtained from XRD; reference columns a^* and c^* represent values for bulk samples. The values for the MnGa phase correspond to stoichiometric (Mn:Ga=1) sample A.

Phase	a [$\text{\AA}$]	c [$\text{\AA}$]	a^* [$\text{\AA}$]	c^* [$\text{\AA}$]	hkl	d [$\text{\AA}$]
MnGa	3.85	3.72	3.89 [26]	3.65 [26]	111	2.197
					002	1.86
Mn ₃ Ga ₅	12.49	25.00	12.66 [22]	24.62 [22]	443	2.13
Mn ₂ Ga ₅	8.82	2.68	8.86 [3]	2.71 [3]	410	2.14
					420	1.97
					221	1.97
MnGa ₄	5.57	-	5.59 [23]	-	220	1.97

TABLE 3: Saturation magnetization, remnant magnetization, and coercive field values for all MnGa on GaN(0001) films extracted from VSM and SQUID hysteresis loops. The values marked with $^\perp$ represent the saturation magnetization for the perpendicular loops.

Sample	M_s [emu/cm ³]	$M_{r\parallel}$ [emu/cm ³]	$H_{c\parallel}$ [kOe]	$M_{r\perp}$ [emu/cm ³]	$H_{c\perp}$ [kOe]
A	371	280	3.2	240	2.4
B	276	196	3.9	190	4.0
C	235	202	3.2	160	2.7
D	195	114	0.8	54	1.2
E	100	63	2.3	53	2.0
F	1627 $^\perp$	24	0.2	143	0.1
G	887 $^\perp$	39	0.9	130	0.1

FIG. 1: (a) θ - 2θ XRD scans for MnGa films grown on GaN(0001); sample compositions range from stoichiometric (Mn:Ga ≈ 1) for sample A to highly Ga-rich (Mn:Ga ≈ 0.42) for sample E. (b) The evolution of d_{111} with sample stoichiometry as determined from shifts in the MnGa111 peak region for the more Mn-rich samples, A, B, and C.

FIG. 2: (a) Room temperature STM image (shown in derivative mode) taken on sample F and acquired at a sample bias $V_s = -300$ mV and tunneling current $I_t = 0.1$ nA; the inset shows the 2×2 reconstruction observed on the lower terraces. (b) STM image taken on the upper region in (a) [$V_s = -300$ mV and $I_t = 0.1$ nA], where row structures with two different periodicities (≈ 9.2 Å and ≈ 12 Å) are mainly visible; enclosed by square and rectangular boxes are different atomic arrangements that appear in addition to the row structures. The inset from (b) represents an STM image taken on sample B, showing the evolution of the structure in (b) as the film thickness increases [$V_s = -100$ mV and $I_t = 0.1$ nA].

FIG. 3: (a) $10 \times 10 \mu\text{m}^2$ AFM image taken on sample G; 3D MnGa islands cover ≈ 46 % of the surface, with the remainder of ≈ 54 % consisting of exposed GaN layers. (a) $10 \times 10 \mu\text{m}^2$ AFM image taken on sample D; it can be seen that as the thickness increases, the film becomes more uniform.

FIG. 4: (a) Room temperature STM image (shown in derivative mode) taken on sample G; the dashed box encloses a more uniform region found on the upper terrace. (b) 3D perspective view of the area from (a), where a large wavelength modulation is visible on the lower terrace. (c) Closer view at the row structure shown on the lower terrace in (a). (d) Image showing a similar area to the one on the higher terrace from (a); dashed boxes emphasize row structures of different periodicities enclosed by bright raised rows. The insets represent line profiles taken along path lines L1 and L2. Images are acquired at $V_s = -100$ mV and $I_t = 0.1$ nA.

FIG. 5: (a) and (b) Room temperature STM images of two areas of sample D, showing similarly reconstructed surfaces, only rotated by $\approx 60^\circ$; dashed boxes in (a) and (b) enclose uniform row arrangements separated by α , and additional measurements indicate that the raised rows are separated by multiples of α . The inset in (a) represents a line profile taken along line path L3. Both images were acquired at $V_s = -130$ mV and $I_t = 0.1$ nA.

FIG. 6: Room temperature VSM plots for samples A, B, C, D, and E showing magnetization vs. applied field for a magnetic field oriented parallel (a) and perpendicular (b) to the samples. (c) and (d) Room temperature SQUID hysteresis loops for samples F and G with magnetic field oriented parallel and perpendicular to the sample surface, respectively; the insets represent closer views at the remnant magnetization and coercivity.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Intensity [a.u.]

Figure2_black_and_white

Figure3_black_and_white

Figure4_black_and_white

Figure5_black_and_white

Figure6_black_and_white

Heteroepitaxial growth by molecular beam epitaxy

Smooth and reconstructed surfaces by *in-situ* scanning tunneling microscopy

Giant perpendicular magnetic anisotropy induced for ultra-thin films