Reconstruction Control of Magnetic Properties during Epitaxial Growth of Ferromagnetic Mn$_{3-\delta}$Ga on Wurtzite GaN(0001)

Erdong Lu, David C. Ingram, and Arthur R. Smith

Nanoscale and Quantum Phenomena Institute, Department of Physics and Astronomy, Ohio University, Athens, Ohio 45701, USA

J. W. Knepper and F. Y. Yang

Department of Physics, The Ohio State University, 191 Woodruff Avenue, Columbus, Ohio 43210, USA

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Binary ferromagnetic Mn$_{3-\delta}$Ga (1.2 < 3 − δ ≤ 1.5) crystalline thin films have been epitaxially grown on wurtzite GaN(0001) surfaces using rf N-plasma molecular beam epitaxy. The film structure is face-centered tetragonal with CuAu type-I ($L_1_0$) ordering with (111) orientation. The in-plane epitaxial relationship to GaN is nearly ideal with [110]$_{\text{MnGa}}$ || [110]$_{\text{GaN}}$ and [112]$_{\text{MnGa}}$ || [1120]$_{\text{GaN}}$. We observe magnetic anisotropy along both the in-plane and out-of-plane directions. The magnetic moments are found to depend on the Mn/(Mn + Ga) flux ratio and can be controlled by observation of the surface reconstruction during growth, which varies from 1 × 1 to 2 × 2 with increasing Mn stoichiometry.

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In the past two decades, there have been many attempts to grow crystalline, tetragonal ferromagnetic (FM) Mn$_x$Ga$_{1-x}$ thin films on a GaAs(100) semiconductor (SC) by molecular beam epitaxy (MBE) [1–6] and, mostly in recent years, to try different ways to fabricate new materials such as Mn-doped GaAs and GaN as dilute FM semiconductors with a potential use in spintronics [7–11]. By comparison, there have been very few attempts to grow epitaxial FM layers on wide band-gap semiconductors such as GaN, although such FM/SC structures have great potential for novel applications, such as for spin light-emitting diodes operating in the blue and ultraviolet (UV) spectral ranges [11,12].

Mn and Ga are known to form different bulk alloy phases, even a quasicrystalline phase, depending on the ratio of Mn to Ga and the temperature during crystal growth and preparation [13–18]. Many phases with Mn greater than or equal to Ga are FM with a high Curie temperature ($T_C$) above room temperature, for example, Mn$_x$Ga$_{1-x}$ with $T_C = 470$ °C, Mn$_3$Ga$_2$ with $T_C = 417$ °C, and MnGa with $T_C > 27$ °C [8,19]. The “δ phase” Mn$_{3-\delta}$Ga, with δ in the range 1.5–1.8, is very promising for spintronic applications due to the high magnetic moment; theoretically, it can be as high as 2.5$\mu_B$. However, to realize the potential of δ-MnGa for blue and UV spintronic devices, it is essential to explore the magnetic and structural properties and their epitaxial growth dependence for thin Mn$_{3-\delta}$Ga layers on wide-band-gap semiconductor (i.e., GaN) and insulating (i.e., MgO or Al$_2$O$_3$) surfaces.

In this Letter, we present new results for Mn$_{3-\delta}$Ga thin layers grown smoothly on w-GaN, both nitrogen-polar (0001) and gallium-polar (0001) substrates. We identify a growth regime which results in near-perfect heteroepitaxy with a well-defined epitaxial film-substrate relationship, a high quality film-substrate interface, and excellent magnetic properties. We show that the film structure can be understood in terms of the (111) face of the well-known face-centered tetragonal (fct) CuAu type-I ($L_1_0$) model for δ-MnGa [13]. While we report magnetic properties of these layers as high as any previously reported values for Mn$_{3-\delta}$Ga, we furthermore show that the magnetic properties can be tuned during MBE growth by monitoring the surface structure and adjusting the flux ratio.

The experiments are performed in a custom-designed, ultrahigh vacuum (UHV) scanning tunneling microscope (STM)/MBE system having Mn and Ga effusion cells and a radio-frequency (rf) nitrogen ($N_2$) plasma source. Mn and Ga fluxes are measured using a quartz crystal thickness monitor. Reflection high energy electron diffraction (RHEED) is used to monitor the growth surface.

Ga-polar substrates used were w-GaN grown on sapphire [Al$_2$O$_3$(0001)] using metal-organic chemical vapor deposition by a commercial vendor, whereas the N-polar substrates were grown on Al$_2$O$_3$(0001) in the lab using rf N-plasma MBE. The Ga-polar substrates were treated (keeping the same polarity) in vacuum by either heating to 650 °C or by growing a fresh 50-nm layer of GaN. N-plasma GaN growth conditions were $T_{sub} = 650$ °C, $P_{N_2} = 9.1 \times 10^{-6}$ Torr, and Ga flux $J_{Ga} = 3.87 \times 10^{14}/\text{cm}^2\text{ sec}$. Following substrate preparation, the substrate temperature was set to $T_{sub} = 250$ °C for the Mn$_{3-\delta}$Ga growth. The flux ratio $R_F = J_{Mn}/(J_{Mn} + J_{Ga})$ was set to achieve a particular stoichiometry within the range of 0.5–0.6, corresponding to a Mn:Ga ratio in the range 2:2–3:2.

Here we focus on two cases, one with $R_F = 0.5$ for Mn:Ga = 1:1(δ = 2) and one with $R_F = 0.55$ for Mn:Ga = 1.22:1(δ = 1.78). Other samples were grown with $R_F = 0.60$, finding similar results as for 0.55. For $R_F = 0.5$, the fluxes of Mn and Ga—$J_{Mn}$ and $J_{Ga}$—are both set at $2.87 \times 10^{14}/\text{cm}^2\text{ sec}$. For $R_F = 0.55$, the fluxes are set at $J_{Mn} = 2.87 \times 10^{14}/\text{cm}^2\text{ sec}$ and $J_{Ga} = 2.35 \times 10^{14}/\text{cm}^2\text{ sec}$. Following Mn$_{3-\delta}$Ga growth, the samples are transferred under UHV to the in situ STM. Samples are...
analyzed ex situ using x-ray diffraction (XRD), Rutherford backscattering spectroscopy (RBS), and vibrating sample magnetometry (VSM).

Figures 1(a) and 1(b) show typical RHEED patterns for a w-GaN(0001) surface just after growth of a fresh 50 nm GaN layer followed by cooling down to the Mn$_{3−δ}$Ga growth temperature $T_{5,\text{MnGa}} = 250$ °C. The apparent Ga-polar, pseudo-\(1 × 1\) reconstruction suggests a smooth GaN(0001) surface [20].

RHEED patterns of the subsequent Mn$_{3−δ}$Ga layer, grown using $R_F = 0.55$, along different azimuths are shown in Figs. 1(e)–1(f). At the initial stage of Mn$_{3−δ}$Ga growth along the GaN[1120] azimuth, as seen in Fig. 1(e), we note that 6× diffraction lines appear. After only 5–10 s of growth, the RHEED pattern evolves to that of the Mn$_{3−δ}$Ga(111) surface, as seen in Fig. 1(d) in the direction of [1100] of GaN, which has already become the [110] direction of Mn$_{3−δ}$Ga. After a full 1 monolayer of Mn$_{3−δ}$Ga growth, the RHEED patterns evolve to the 2× patterns shown in Figs. 1(e) and 1(f), taken after the film had reached a final thickness of \(\sim 1100\) Å. For Mn$_{3−δ}$Ga growth with a smaller flux ratio ($R_F = 0.5$), the growth evolution is the same except that there are no 2× streaks, as shown in Figs. 1(g) and 1(h).

The stoichiometry obtained at $R_F = 0.55$ was found to have Mn:Ga \(\sim 1.22−1.5:1\), corresponding to \(δ\) in the range 1.5–1.78 or, equivalently, Mn/(Mn + Ga) composition in the range 0.55–0.6. Such values are very consistent with previous measurements for CuAu-$L_1_0$-type fct Mn$_{3−δ}$Ga samples prepared using bulk synthesis [13].

In our experiments, the Mn$_{3−δ}$Ga RHEED patterns are always streaky for $R_F$ within the range 0.5–0.6 and from the very beginning of MnGa growth, indicating high quality epitaxy of the Mn$_{3−δ}$Ga layer on the GaN substrate. Comparing Figs. 1(e) and 1(f) with Figs. 1(a) and 1(b), the in-plane symmetries of the Mn$_{3−δ}$Ga layer are clearly reversed from those of the GaN(0001) substrate, corresponding to a 30° rotation of the hexagonal lattice. We thus derive an epitaxial relationship of the Mn$_{3−δ}$Ga layer with the GaN(0001) substrate. Shown in Fig. 2(a) is a model of the Ga-terminated, w-GaN(0001) surface lattice. Similarly, shown in Fig. 2(b) is a three-dimensional model of the Mn$_{3−δ}$Ga fct lattice [13]. From this 3D model, one can derive the top view model of the Mn$_{3−δ}$Ga(111) surface, as shown in Fig. 2(c). It consists of an alternating Mn and Ga row structure.

By overlaying the Mn$_{3−δ}$Ga(111) lattice onto the GaN(0001) lattice, as shown in Fig. 2(d), we find a nearly perfect epitaxial relationship, with a 30° rotation between the two lattices. This interface model involves the smallest number of high symmetry bonding sites, including Ga bridge, Mn bridge, and Mn atop sites, resulting in an ideal epitaxial fit. Interchange of Ga and Mn overlayer atoms would result in a similar model without affecting the RHEED symmetry.

From the RHEED results, the in-plane lattice parameters of the Mn$_{3−δ}$Ga layers are computed to be $a_1 = 2.67$ Å and $a_2 = 2.76$ Å, in good agreement with values deduced...
from the known fct lattice parameters [13], which are \( a_1 = \text{Mn-Ga distance} = 2.67 \, \text{Å} \) and \( a_2 = \text{Mn-Mn or Ga-Ga distance} = 2.756 \, \text{Å} \). Negligible difference was found among samples grown with different \( R_F \).

Thus, we have an epitaxial \( \text{Mn}_3\text{Ga} \) layer having the [111] axis perpendicular to the (0001) GaN surface and with the epitaxial relationship \( \text{Mn}_3\text{Ga}(111)[1\bar{1}0] \parallel \text{GaN}(0001)[1\bar{1}0] \parallel \text{Mn}_3\text{Ga}(111)[1\bar{1}2] \parallel \text{GaN}(0001)[\bar{1}10] \). The growth orientation of the \( \text{Mn}_3\text{Ga} \) film was confirmed by XRD and RBS ion channeling.

To achieve the high quality \( \text{Mn}_3\text{Ga}(111) \) epitaxial growth on \( \text{w-GaN}(0001) \) presented here, it is crucial to hold \( T_{\text{sub}} \) at 250 °C for growth with \( R_F \) varying in the range of 0.5–0.6. In this range, the sharp and streaky 6× RHEED pattern always appears at the initial stage of the growth. Such a streaky, reconstructed RHEED pattern suggests a smooth and abrupt \( \text{Mn}_3\text{Ga}/\text{GaN} \) interface, which is a key advantage since one of the most desirable properties for any FM/SC system is a smooth and abrupt interface. In most conventional FM/III–V SC systems, interface roughness and interdiffusion are serious problems which typically lead to the formation of interface compounds, even antiferromagnetic (AFM) interface layers. The \( \text{Mn}_3\text{Ga}/\text{GaN} \) interface avoids both of these problems. This is due to (a) the strong and stable Ga-N bond which prevents reaction between the anion (N) and the FM overlayer; (b) the chemical compatibility of \( \text{Mn}_3\text{Ga} \) with the well-known gallium-rich surface of MBE-grown \( \text{w-GaN}(0001) \) [20] which further prevents reactions with N; (c) the high immiscibility of Mn and Ga which further prevents Mn from entering into the GaN layer; and (d) the ideal \( \text{Mn}_3\text{Ga}/\text{GaN}(0001) \) epitaxial relationship which prevents interface roughness and promotes two-dimensional epitaxy.

An STM image of the smooth \( \text{Mn}_3\text{Ga}(111) \) surface grown with \( R_F = 0.55–0.6 \), of size \( 300 \, \text{Å} \times 300 \, \text{Å} \) and including several atomic-height terraces, is shown in Fig. 3(a). The height of an individual step is measured to be \( h = 2.23 \, \text{Å} \), in good agreement with the \( d \) spacing between \( \text{Mn}_3\text{Ga}(111) \) planes obtained from XRD (\( \sim 2.20 \, \text{Å} \)). It is also consistent with the CuAu-L10-type fct \( \text{Mn}_3\text{Ga}(111) \) interplanar spacing. Zooming in to a smaller area, as shown in Fig. 3(b), the real-space atomic image corresponding to the \( \frac{1}{2} \)-order RHEED streaks is observed. Although the corrugation is not large, we find a hexagonlike lattice with spacing \( 2 \times 2.7 \, \text{Å} = 5.4 \, \text{Å} \).

Thus, we find that the stoichiometry can be determined from the surface reconstruction: \( 1 \times 1 \Rightarrow 1:1 \, \text{Mn to Ga} \), and \( 2 \times 2 \Rightarrow 3 - \delta:1 \, \text{Mn to Ga} \), with \( \delta \) in the range 0–2. The \( 2 \times 2 \) is therefore an indicator of higher Mn incorporation and other important layer properties.

To understand the origin of the \( 2 \times 2 \) structure, we reconsider the \( 1 \times 1 \) occurring for lower flux ratio \( R_F = 0.5 \); at the surface, we find alternating rows of Mn and Ga atoms, as shown in Fig. 3(c). The \( 2 \times 2 \), occurring for \( R_F > 0.5 \), is then obtained by replacing every other Ga atom with a Mn atom, as shown in Fig. 3(d). If this MnGa replacement is continued into the bulk, a Mn:Ga = 3:1 stoichiometry would result, equivalent to the MnGa (\( \delta = 0 \)) phase \( \Rightarrow 75\% \) Mn content. For \( 0.5 < R_F < 0.75 \), we expect only partial replacement, consistent with our RHEED results for Mn:Ga = 1.22–1.5:1 (\( R_F = 55\%–60\% \)), in which we observe weak \( \frac{1}{2} \)-order streaks.

The magnetic properties of the epitaxial \( \text{Mn}_3\text{Ga} \) films on both Ga-polar and \( N \)-polar GaN substrates were investigated by VSM at 25 °C. All films exhibited magnetic anisotropy, based on comparison of VSM hysteresis loops along the perpendicular [111] and parallel [112] and/or [110] directions. The saturation magnetization \( M_s \), remnant magnetization \( M_r \), and coercivity \( H_c \) vary for different samples depending on their compositions. In particular, \( M_s \) was found to vary from 250 to 510 emu/cm³. Previous theoretical and experimental work has confirmed that \( \text{Mn}_3\text{Ga} \) is ferromagnetic for Mn content in the range 50%–74.7% [1–3,5,21,22]. Van Roy et al. [2] reported \( M_s \) decreasing from 510 to 450 emu/cm³ and \( T_C \) increasing with increasing Mn content in the range 56%–59%. Tanaka et al. [3] reported two samples, one having \( M_s = 414 \, \text{emu/cm³} \) with \( T_C = 327 \, \text{°C} \) at 56% Mn and another having \( M_s = 390 \, \text{emu/cm³} \) with \( T_C = 373 \, \text{°C} \) at 59% Mn. Also, \( M_s = 460 \, \text{emu/cm³} \) at 62% Mn was reported by Krishnan [5].

By tuning the reconstruction during MBE growth, we can control the magnetic properties of the \( \text{Mn}_3\text{Ga} \) layers grown on \( \text{w-GaN} \) wide band-gap semiconductor and sapphire substrates. Figure 4 shows magnetization vs applied magnetic field for magnetic fields applied both perpendicular
l lar and parallel to the Mn$_{3-x}$Ga(111) thin film surfaces. The hysteresis loops clearly show magnetic anisotropy of the Mn$_{3-x}$Ga thin films for both the 1×1 and 2×2 reconstructions. For the 1×1-reconstructed Mn$_{3-x}$Ga(111) with 50% Mn concentration as seen in Fig. 4(a), $M_r = 375$ emu/cm$^3$; in this case, $M_r = 207$ emu/cm$^3$ and $H_c = 1.913$ kOe for the in-plane loop, whereas $M_r = 104$ emu/cm$^3$ and $H_c = 1.528$ kOe for the out-of-plane loop. For the 2×2-reconstructed Mn$_{3-x}$Ga(111) at 55% Mn concentration as seen in Fig. 4(b), $M_r = 510$ emu/cm$^3$; in this case, $M_r = 423$ emu/cm$^3$ and $H_c = 2.168$ kOe for the in-plane loop, whereas $M_r = 247$ emu/cm$^3$ and $H_c = 1.928$ kOe for the out-of-plane loop. All of our samples show similar anisotropy of $M_r$ and $H_c$, confirming the epitaxial, crystalline quality of our Mn$_{3-x}$Ga thin films on w-GaN substrates.

The deduced magnetic moments in our Mn$_{3-x}$Ga thin films vary from $m = 0.76\mu_B$/Mn atom at 50% Mn content to $m = 1.88\mu_B$/Mn atom at 55% Mn content. For 60%, we measured only 0.85$\mu_B$/Mn atom. Although our experimental moments are among the highest reported, our highest measured value is still lower than the theoretical values of 2.33$\mu_B$ and 2.42$\mu_B$ per Mn atom for 6-MnGa (Mn:Ga = 1:1) predicted by Yang et al. [22] and by Sakuma [21], respectively. As it is reported experimentally that for Mn/(Mn + Ga) fraction ≥75%, the magnetic moment is very small due to AFM interactions [2], our measured reduction of $m$ over the range from 55% to 60% Mn content may be due to the onset of AFM interactions.

In conclusion, high quality epitaxial growth of ferromagnetic layers of Mn$_{3-x}$Ga with ideal lattice matching having a (111) orientation to w-GaN(0001) or (0001) and an abrupt interface is reported. The magnetic properties are tuned by adjusting the reconstruction during growth which affects the composition, and the composition change with Mn flux is shown to be detected by the 2×2 reconstruction. Mn atoms fill into Ga sites in an ordered arrangement, resulting in Mn:Ga > 1:1 and up to 3:1 at complete Mn filling. The results suggest a gradual transition from the fct (111)-oriented structure to a hexagonal structure. The Mn$_{3-x}$Ga/GaN structures are promising for spintronic applications in integrated magnetic-semiconductor devices.

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