Mater. Res. Soc. Symp. Proc. Vol. 1118 © 2009 Materials Research Society 1118-K06-06

Delta-phase manganese gallium on gallium nitride: a magnetically tunable spintronic system

Kangkang Wang[1], Abhijit Chinchore[1], Wenzhi Lin[1], Arthur Smith[1] and Kai Sun[2]
[1]Department of Physics and Astronomy, Ohio University, Athens, OH 45701, U.S.A.
[2]Department of Materials Sciences and Engineering, University of Michigan, Ann Arbor, MI 48109, U.S.A.

ABSTRACT

Ferromagnetic delta-phase manganese gallium with Mn:Ga ratio between 1:1 to 1.5:1 is grown on wurtzite gallium nitride and scandium nitride substrates, using molecular beam epitaxy. The dependencies of growth properties, e.g. interface formation, surface reconstruction and crystalline quality, on substrate crystallographic structure and polarity are investigated. Results suggest that for growth on wurtzite GaN, Ga-polar surface promotes quicker interface formation, and also results in better crystalline quality of the MnGa film, as compared to N-polar. The crystal orientation and magnetic anisotropy are found to be different than those grown on cubic scandium nitride substrates.

INTRODUCTION

Ferromagnetic metal/semiconductor layered structures are of great interest due to their potential for novel spintronics applications such as spin light-emitting diodes[1]. Delta phase manganese gallium, a ferromagnetic alloy with high magnetic moments (~2.51 μ_B/Mn atom[2]) and Curie temperature above room temperature, appears to be a promising candidate for such applications. There have been several reports[3,4] on epitaxial growth of δ-MnGa on zinc-blende GaAs(001) substrates, where perpendicular magnetization was found. Furthermore, it was recently reported[5] that ferromagnetic δ-MnGa can be grown epitaxially on top of wide band-gap Ga-polar wurtzite GaN(0001), with controllable magnetism by adjusting slightly the Mn:Ga atom concentration. While many important spintronics properties, such as spin injection efficiency and magnetic anisotropy, strongly depend on the interface abruptness and crystallographic structure of the film, further experiments targeting a better understanding of these issues, especially for MnGa/GaN system, appear to be still lacking.

Here we further investigate the substrate and polarity dependencies of the growth and magnetic properties of the MnGa film, with a focus on the interface formation. We will show that, compared to N-polar wurtzite GaN substrates, Ga-polar appears to promote quicker formation of the new δ-MnGa lattices, hence resulting in a more well-defined, abrupt interface. This advantage also continues into thicker films, yields smoother surface as well as better crystallinity. These differences could be due to the different chemical environments on different polarities of GaN surfaces. A comparison to the growth on cubic-structured scandium nitride substrates reveals dramatically different magnetic anisotropies, resulting from the different orientation of the film.

EXPERIMENT

Experiments are carried out in a custom-designed, ultra-high-vacuum (UHV) molecular beam epitaxy (MBE) / scanning tunneling microscope (STM) system, with a base pressure ~2E-

10 Torr. The MBE chamber is equipped with Ga, Mn, and Sc effusion cells as well as a nitrogen plasma source. A quartz crystal monitor is used for flux calibration of the effusion cells. The growth is monitored in real-time using reflection high energy electron diffraction (RHEED). After growth, samples are transferred *in-situ* for STM measurements and *ex-situ* for atomic force microscopy (AFM), x-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), and vibrating sample magnetometry (VSM) measurements.

For growth of δ-MnGa on N-polar wurtzite GaN substrates, commercially available sapphire (0001) is used for the starting substrate. After ultrasonicating in solvents and introducing into the vacuum, sapphire substrates are first flashed to 1000 ^{o}C under nitrogen plasma for 30 minutes, then cooled down and maintained at 650 ^{o}C for GaN growth. Slight Ga-rich growth condition is used in order to achieve a smooth surface[6]. Growth is stopped when the GaN film thickness reaches ~100 nm. Then sample temperature is lowered to room temperature to check the surface reconstructions. Finally, the sample is heated up to 250 ^{o}C for initiating MnGa growth. Mn and Ga are co-deposited onto the surface with Mn:Ga ratio controlled at about 1.2:1.

For growth on Ga-polar GaN substrates, the only difference is the preparation of the substrate. Commercial MOCVD grown GaN(0001) is used as starting substrates. After annealing in UHV at 600 ^{o}C for 30 minutes, a fresh layer of GaN is grown on top of it which follows the substrate polarity. The subsequent MnGa growth conditions are the same as the ones used on N-polar.

To explore the growth properties of MnGa film on cubic-structured substrates, ScN(001) is prepared. These substrates are grown using MBE in scandium rich regime, on top of MgO(001) substrates. The procedure is same as described by Smith *et al.* [7]

RESULTS AND DISCUSSIONS

MnGa grown on wurtzite GaN surface

In general, MnGa grown with Mn to Ga ratio near 1.2:1 on top of wurtzite GaN surfaces, either Ga-polar (0001) or N-polar (000$\underline{1}$), exhibits an epitaxial growth and results in a highly oriented crystalline film. From XRD measurements and RHEED streak spacing measurements, the phase can be determined to be delta-phase, which has a body centered tetragonal structure, with the body-center atom different from the corner atoms. Also the surface of the film is determined to be (01$\underline{1}$) plane of δ-MnGa, which has a slightly-distorted hexagonal in-plane structure. The epitaxial relationship of MnGa lattice to the GaN substrate can be derived from RHEED measurements as $[011]_{MnGa}//[11\underline{2}0]_{GaN}$ and $[111]_{MnGa}//[1\underline{1}00]_{GaN}$, as shown in Fig.1.

In-plane atom spacings *a1* and *a2* of the MnGa lattice are calculated from RHEED spacing measurements to be a1=2.67 Angstrom and a2= 2.76 Angstrom [5], which gives a nearly perfect match to the underlying hexagonal GaN lattice having a=2.76 Angstrom. These values are also consistent with reported bulk lattice values for δ-MnGa[4]. Details of lattice evolution and these epitaxial relationship derivations will not be given here since these findings are similar to those reported by E. D. Lu *et al*[5], except that there MnGa lattice is viewed as L10-CuAu crystal structure (similar to face centered tetragonal) and named *3-δ* phase instead of *δ* phase. Also because of the different choice of lattice basis vectors, indices for lattice planes and directions are labeled differently. For example here [01$\underline{1}$] direction corresponds to [111] direction in Lu *et.al* 's paper.

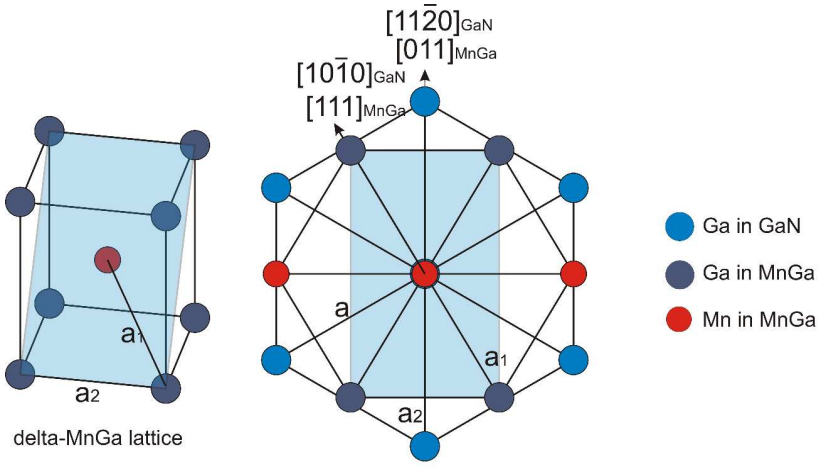

Fig.1 schematics showing the epitaxial relationship between δ-MnGa and GaN lattices: $[011]_{MnGa}//[0001]_{GaN}$ or $[000\underline{1}]_{GaN}$, in plane lattice relationship: $[011]_{MnGa}//[11\underline{2}0]_{GaN}$ and $[111]_{MnGa}//[1\underline{1}00]_{GaN}$.

Fig.2 shows a comparison of the RHEED evolution during the growth of MnGa on two different polarities of wurtzite GaN, namely Ga-polar (0001) face and N-polar (000-1) face. Judging from the RHEED patterns, the starting Ga-polar GaN surface has a "1×1" reconstruction, while N-polar GaN surface exhibits a 3×3 reconstruction, which are both consistent with the Ga-rich growth regime[8]. The streaky bright RHEED patterns indicate smooth, well-ordered GaN surfaces.

After just one monolayer of MnGa deposition, the structure grown on Ga-polar GaN has already transformed into δ-MnGa, while that grown on N-polar is still in transition. When the thickness of MnGa has reached about 100 monolayers, streakier and stronger primary streaks for Ga-polar case indicate a better crystallinity and smoother surface when compared to the N-polar case.

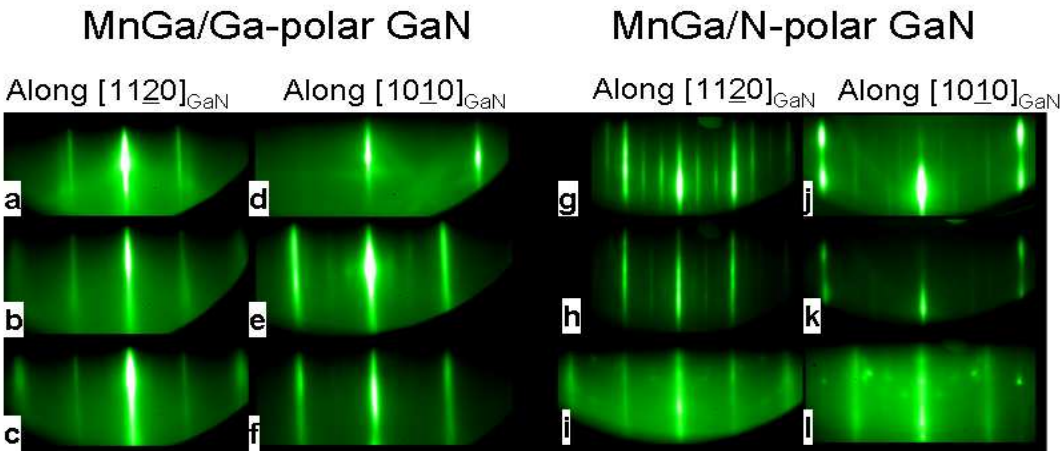

Fig.2 RHEED evolution of δ-MnGa grown on wurtzite GaN. Different columns are taken along different in-plane directions, a to c: $[11\underline{2}0]_{GaN(0001)}$, d to f: $[10\underline{1}0]_{GaN(0001)}$, g to i: $[11\underline{2}0]_{GaN(000\underline{1})}$, j to l: $[10\underline{1}0]_{GaN(000\underline{1})}$. Different rows are taken at different thicknesses of MnGa film, from top to bottom: before MnGa deposition, one monolayer of MnGa deposited, 100 monolayers of MnGa deposited.

The quick transition from Ga-polar GaN lattice to δ-MnGa lattice suggests an abrupt interface, which is also confirmed by HR-TEM measurements. Fig.3 shows two typical cross-sectional TEM images taken on two different polarities. While both samples show a nice, well-defined interface, the one grown on Ga-polar GaN appear to have more abrupt interface. This property is desired in applications such as spin-injection from ferromagnet into semiconductor, since it reduces interface diffusion and increases injection efficiency.

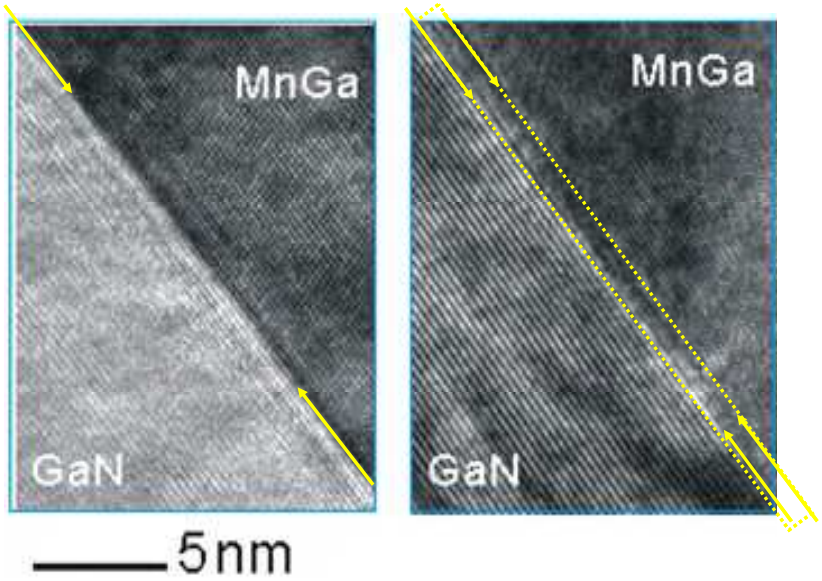

Fig.3 Comparison of two typical images on MnGa/GaN interface obtained using cross-sectional HR-TEM. Polarities of GaN used are Ga-polar for the left, and N-polar for the right, respectively.

The MnGa films grown on Ga-polar GaN substrates were not only found to have sharper interfaces, but also better bulk crystallinity and surface smoothness. As shown in Fig.4, AFM images were acquired on two different sets of samples.

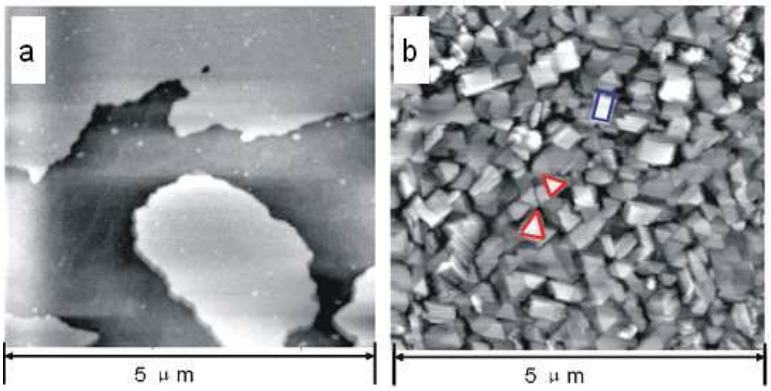

Fig.4 Comparison of AFM images on MnGa/GaN films. Polarities of GaN used are for (a) Ga-polar, and for (b) N-polar, respectively. Image size: 5×5 micrometers. Grey level: 20 nm for both images.

Large, flat terraces were commonly found on MnGa/Ga-polar GaN whereas small, triangular and rectangular shaped island structures were found on MnGa/N-polar GaN. This is

consistent with the streakier, brighter RHEED patterns observed at the last stages of growth of MnGa/Ga-polar GaN (Fig.2 c,f,i,l)

The quicker transformation from GaN lattice into δ-MnGa lattice in the case of Ga-polar *w*-GaN could be due to the more dynamic, excess Ga double layer of the "1×1" surface[8]. These Ga ad-atoms are highly mobile compared to the 3×3 reconstructed Ga terminated N-polar surface. This could help forming the new MnGa lattice quicker, and lead to a more abrupt interface, and eventually better crystallinity of the entire film.

Comparing to MnGa/ScN(001)

In order to explore the dependence of MnGa growth on substrate crystallographic symmetry, cubic structured ScN(001) was prepared and used as a substrate. ScN is a semiconductor with both a direct and an in-direct band-gap. The crystal structure of ScN is rock-salt with a lattice constant of 4.501 Angstrom[7].

Under the same MnGa film growth conditions as MnGa/GaN samples(flux ratio, substrate temperature), the primary phase for MnGa grown on ScN(001) is also found to be δ-phase. While details of these experiments, such as epitaxial relationship and magnetism measurements will be given elsewhere, the main differences as compared to using three-fold symmetric GaN substrates are as following: 1) MnGa is found to grow along [001] direction on ScN(001) as compared to [01$\bar{1}$] direction when grown on three-fold symmetric GaN (0001) or (000$\bar{1}$) surfaces. 2) Strong magnetic anisotropy is found, with easy axis lying *out-of-plane* (see Fig.5). The ratio of *out-of-plane* to *in-plane* remnant magnetization is found to be as large as 5:1, larger than the values for MnGa/GaN reported by E. D. Lu *et al.* [5] (1.7~1.8).

The effect of the ambient conditions (air atmosphere) on the anisotropy seen here is unknown, although we do not see any obvious signs of oxidation of the films; therefore, we do not expect that the results are significantly perturbed by the atmosphere.

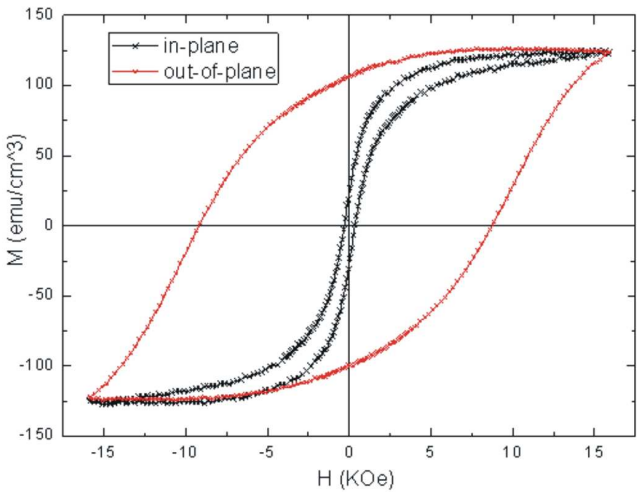

Fig.5 Magnetic hysteresis loop obtained on MnGa/ScN(001) using vibrating sample magnetometer at ambient conditions.

Assuming the easy axis for unstrained bulk δ−MnGa is along its c-axis, for MnGa/GaN case, the easy-axis would be canted from the surface plane and lie between *in-plane* and *out-of-plane* directions. On the other hand, for MnGa/ScN(001), the easy axis lies along *out-of-plane*

direction. This difference in crystallographic orientation is consistent with the different magnetic anisotropy observed.

CONCLUSIONS

The dependencies of δ−MnGa growth on substrate polarities (for wurtzite GaN) and substrate crystal structure are investigated. It is found that, comparing to 3×3 reconstructed N-polar *w*-GaN surface, Ga-polar *w*-GaN promotes a quicker formation of δ−MnGa lattice, resulting in more abrupt interface and also better crystallinity of MnGa film. The dynamic Ga double layer on Ga-polar surface could account for this difference. Different growth direction and magnetic anisotropy is found when growing MnGa onto cubic structured ScN(001).

ACKNOWLEDGMENTS

This work is supported by DOE (Grant No. DE-FG02-06ER46317) and NSF (Grant No. 0730257). Equipment support from ONR is also acknowledged.

REFERENCES

1. S.A. Wolf, D.D. Awschalom, R.A. Buhrman, J.M. Daughton, S. von Molnar, M.L. Roukes, A.Y. Chtchelkanova, and D.M. Treger, Science **294**, 1488 (2001).
2. A. Sakuma, J. Magnetism and Magnetic Materials **187**, 105 (1998).
3. M. Tanaka, J.P. Harbison, J. DeBoeck, T.Sands, B. Philips, T.L. Cheeks and V.G. Keramidas, Appl.Phys.Lett. **62**, 1565 (1993).
4. W. Van Roy, H. Akinaga, S. Miyanishi, K. Tanaka and L.H. Kuo, Appl.Phys.Lett. **69,** 711 (1996).
5. E.D. Lu, D.C. Ingram, A.R. Smith, J.W.Knepper and F.Y.Yang, Phys.Rev.Lett. **97**, 146101 (2001).
6. A.R. Smith, R.M. Feenstra, D.W. Greve, M.S. Shin, M. Skowronski, J.Neugebauer, J.E. Northrup, Surf.Sci. **423,** 70(1999)
7. A.R. Smith, H.A. Al-Brithen, D.C. Ingram and D. Gall, J.Appl.Phys. **90**, 1809 (2001).
8. A.R. Smith, R.M. Feenstra, D.W. Greve, M.S. Shin, M. Skowronski, J.Neugebauer, J.E. Northrup, J.Vac.Sci.Tech.B. **16,** 2242 (1998)