Epitaxial growth of ferromagnetic δ-phase manganese gallium on semiconducting scandium nitride (001)

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Abstract

Ferromagnetic δ-phase manganese gallium layers with $Mn/(Mn + Ga) = 60\%$ have been successfully grown on ScN(001) by molecular beam epitaxy, expanding possibilities for ferromagnetic layers on nitride semiconductors. The *in-plane* epitaxial relationship of manganese gallium with respect to scandium nitride is determined to be $[100]_{MnGa}//[110]_{ScN}$ and $[110]_{MnGa}//[100]_{ScN}$. Vibrating sample magnetometry measurements indicate *out-of-plane* magnetization of the film, suggesting strong magnetic anisotropy along the manganese gallium c-axis.

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I. INTRODUCTION

Ferromagnetic thin films on semiconductor bi-layer structures have attracted significant interest in the past two decades due to their important applications in spintronics, such as spin-injection and spin light-emitting diodes[1, 2].

A very promising ferromagnetic material is body-centered tetragonal (bct) structure δ-Mn_xGa_{1-x} with x ranging from 50% to 70%. Epitaxial growth of δ-MnGa on zinc-blende GaAs and also the growth of MnGa/GaAs/MnGa heterostructures have been reported by several groups[2, 3]. Recently, direct measurements of spin injection from δ-MnGa into (Al,Ga)As p-i-n light-emitting diodes have also been reported[2]. In the nitride systems, Lu *et al.* have recently reported epitaxial growth of δ-MnGa on wurtzite GaN(0001) with controllable magnetic properties via controlling the Mn:Ga flux ratio and monitoring the surface reconstructions during growth[4].

Encouraged by these promising results, it is also desirable to explore growth of this magnetically controllable ferromagnetic δ-MnGa layer on top of cubic nitride substrates such as rock-salt (face-centered cubic) structure ScN. Scandium nitride is a transition metal nitride semiconductor having a direct band gap of 2.15 eV, an indirect band gap of 0.9 eV, and a lattice constant of 4.50 Å.[5] Despite clear limitations for room-temperature light-emitting applications, such ferromagnet on indirect-gap semiconductor bilayers are nevertheless highly interesting systems for spin-injection and spin current formation in potential future spin devices.

In the case of ScN, its octahedral bonding configuration could result in a very well-defined film/substrate interface. Furthermore, epitaxial growth of atomically smooth ScN(001) films on MgO(001) substrates has been demonstrated by Al-Brithen *et al.* using scanning tunneling microscopy.[5–7]. Combining these advantages with other attractive properties of ScN such as its high melting temperature of over 2600 $°C$[8] and high hardness ($H \sim 21GPa$)[9] makes the δ-MnGa/ScN(001) system an intriguing one to investigate.

In this paper, we present new results on epitaxial growth of ferromagnetic δ-MnGa on semiconducting ScN. From the obtained diffraction data, we derive the epitaxial relationship of δ-MnGa grown on ScN, and we also investigate the magnetic properties of the resulting film.

II. EXPERIMENTS

Our samples are prepared in an ultra-high-vacuum (UHV) chamber equipped with Mn, Ga, and Sc effusion cells and a radio-frequency (rf) nitrogen (N_2) plasma source. Growth is monitored by reflection high energy electron diffraction (RHEED) in real-time. After growth, the samples are analyzed *ex-situ* using x-ray diffraction (XRD), Rutherford backscattering spectroscopy (RBS), and vibrating sample magnetometry (VSM).

Commercially available MgO(001) substrates are used in our experiments. After ultra-sonicating in acetone and iso-propanol, the substrates are introduced into vacuum and heated to 1000 $°C$ under N-plasma for 30 minutes in order to obtain a smooth, crystalline starting surface. The substrate temperature is then lowered to 750 $°C$ for growth of the ScN film. The ScN film is grown in N-rich regime, with Sc flux about $7.0 \times 10^{13}/cm^2s$ and $P_{N_2} = 1.1 \times 10^{-5}\ Torr$, to a thickness of 10 nm. These conditions lead to epitaxial growth of stoichiometric ScN with surface having square-shaped plateaus and atomically smooth terraces[7].

After the ScN growth, the substrate temperature is further lowered to 250 $°C$ to initiate δ-MnGa growth. The flux ratio $R_F = J_{Mn}/(J_{Mn}+J_{Ga})$ is set to 0.6 during growth, targeting a Mn:Ga ratio of 1.5:1. A total thickness of 130 nm of MnGa is grown.

III. RESULTS AND DISCUSSIONS

The RHEED evolution of the growth is shown in Fig. 1. Fig. 1(a) and Fig. 1(b) are taken on MgO(001) after annealing, at a substrate temperature of 750 $^{\circ}C$. Clear streaks indicate good substrate crystallinity. After growth of ScN, RHEED patterns evolve into Fig. 1(c) and Fig. 1(d), which are taken along the same directions as Fig. 1(a) and Fig. 1(b), respectively, at the same temperature. By measuring the spacing between the two primary streaks in Fig. 1(c), the lattice constant of our ScN film is determined to be 4.43 Å, slightly lower than the bulk relaxed value of 4.501 Å.[10] The epitaxial relationship of the ScN(001) to the MgO(001) is $[100]_{ScN}//[100]_{MgO}$ and $[110]_{ScN}//[110]_{MgO}$ [6]. The RHEED patterns suggest a well-ordered ScN(001) surface to begin MnGa growth.

After a few minutes of δ-MnGa growth, the RHEED patterns evolve into Fig. 1(e) and Fig. 1(f), which are taken along the same directions as the ones above, at growth temperature of 250 $^{\circ}C$. Primary streaks are clearly observed, along with some fractional-order streaks, in both azimuths. The streaky, bright RHEED patterns indicate a highly crystalline film and smooth surface.

Since the δ-MnGa is bct, the ratio of [100] primary streak spacing to [110] primary streak spacing is $1/\sqrt{2}$. Fig. 1(e) can therefore be determined to be the [110] azimuth of the δ-MnGa film, and Fig. 1(f) can be determined to be the [100] azimuth. Hence we can derive the epitaxial relationship of the δ-MnGa to ScN(001) to be $[110]_{MnGa}//[100]_{ScN}$ and $[100]_{MnGa}//[110]_{ScN}$. Fig. 2 shows an overlay model illustrating this epitaxial relationship, which shows that the δ-MnGa conventional lattice is rotated by 45° with respect to the underlying ScN conventional lattice.

From the RHEED streak spacing measurements, the *in-plane* lattice constant a of the δ-MnGa film is determined to be 2.79 Å, in good agreement with, if only slightly larger than, other reported findings (2.74-2.76 Å) [3, 11]. In XRD spectra, as shown in Fig. 3, sharp δ-MnGa 001 and 002 peaks are clearly observed along with MgO 002 and ScN 002 peaks, indicating that the c-axis of δ-MnGa is aligned along the growth direction. Using 1.542 Å as the average wavelength of the Cu-$K\alpha$ x-ray, the lattice constant c is calculated to be 3.08 Å. This value is close to the one reported by Tanaka *et.al* (3.1 Å, for reported Mn:Ga ratio = 3:2)[3] but considerably smaller than values reported by VanRoy *et al.* and Palmstrøm *et al.* (3.6-3.7 Å)[2, 11].

RBS measurements confirmed our MnGa film has a Mn:Ga composition ratio of 1.5:1, within an error of 1%. We anticipate that the difference in our c-parameter compared to others (-14%) may be due to different stoichiometry. Such a strong effect can result from vacancy or substitutional ordering, as has been seen in many systems.[14] In the case of MnGa, it is interesting to consider that at Mn:Ga = 1.6:1, a new phase emerges, namely the ζ-phase (Mn_8Ga_5) which has γ-brass cubic structure, consisting of ordered Ga vacancies (vacancies on every 3rd Ga site in all 3 high symmetry directions). We also note that the lattice constant for the ζ-phase Mn_8Ga_5 is 8.9 Å[15] ,which is 3× 2.967 Å, a number intermediate between our measured a and c values, implying a tendency of converting into cubic lattice from tetragonal when Mn concentration is increased.

To further explore possible ordering effects in our sample, we observe strong 3× fractional streaks throughout the growth of MnGa along $[100]_{MnGa}$ [Fig. 1(f)], and weak 2× streaks along $[110]_{MnGa}$ [Fig. 1(e)]. These fractional order streaks are similar to those reported by Van Roy *et.al* [11] on GaAs(001) substrates. Therefore, the 3× does not seem to depend on the stoichiometry or on the c-parameter. On the other hand, the 2× was not observed in a sample grown with Mn:Ga flux closer to 1:1, indicating that it *does* correlate with stoichiometry. Further work will be needed to conclusively determine if the 3× and the 2× are surface or bulk periodicities.

Fig. 4 shows the magnetization as a function of applied magnetic field, acquired with VSM at room temperature, demonstrating strong magnetic anisotropy. The remnant magnetizations for *out-of-plane* and *in-plane* directions, $M_{r\perp}$ and $M_{r\parallel}$, are 106 emu/cm^3 and 20 emu/cm^3, respectively, with a coercivity of 8.8 kOe in the *out-of-plane* direction. This result is consistent with the fact that the long axis of the δ-MnGa tetragonal lattice is also *out-of-plane*. We note that the measured $M_{r\perp}$ value is smaller than previously reported values of 225 emu/cm^3 [3] for δ-MnGa on GaAs. We expect the difference to be related to a strong sensitivity of the magnetization to small changes in stoichiometry over the range 50-60% Mn, as reported by Lu *et al.*[4]

IV. SUMMARY

In conclusion, we have successfully grown ferromagnetic δ-MnGa on semiconducting ScN(001). The growth is very smooth as indicated by RHEED. A well-defined epitaxial relationship is derived, as $[110]_{MnGa}//[100]_{ScN}$ and $[100]_{MnGa}//[110]_{ScN}$, revealing a 45° rotation between the two lattices. VSM measurements reveal an *out-of-plane* magnetization along the film's c-axis. Fine-tuning the stoichiometry is expected to yield much higher magnetization, making the system promising for novel magnetic/semiconductor hybrid devices.

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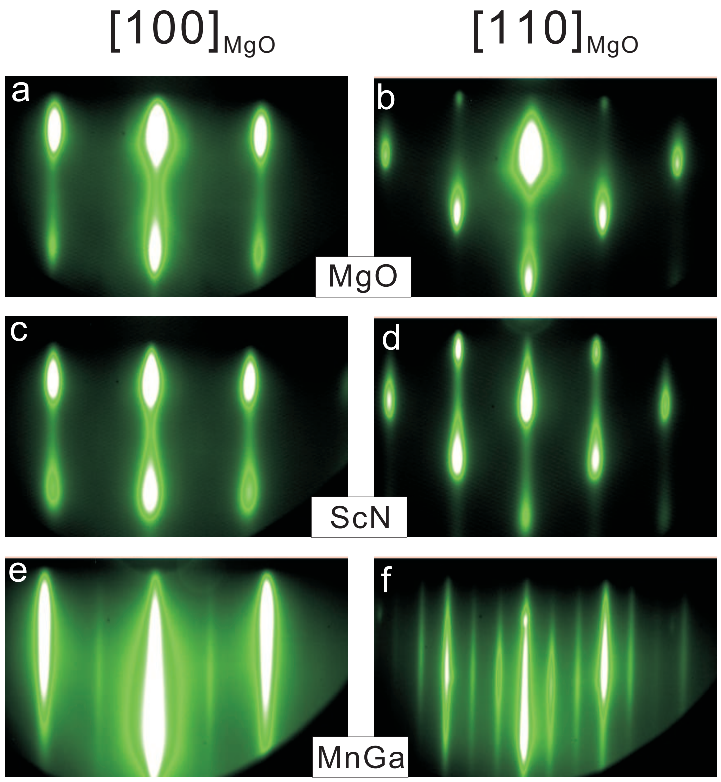

FIG. 1: RHEED patterns: left column along [100] of MgO(001); right column along [110] of MgO(001). (a),(b) MgO(001) after annealing, taken at 750 $°C$. (c),(d) 10 nm ScN(001) grown at 750 $°C$. (e),(f) 130 nm δ-Mn_3Ga_2 grown at $T_S = 250$ $°C$. Note that the direction has now changed to $[110]_{MnGa}$ and $[100]_{MnGa}$ for (e) and (f), respectively.

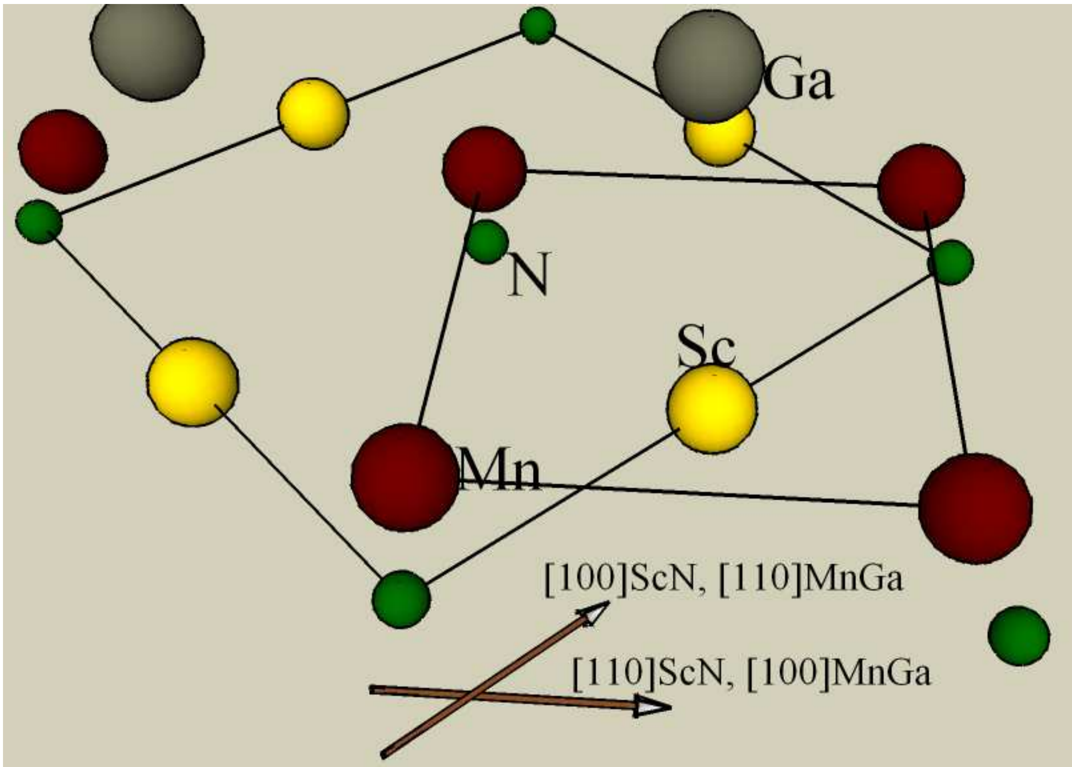

FIG. 2: 3D schematic showing derived epitaxial relationship of δ-MnGa(001) to ScN(001). Squares indicate the conventional unit cells of the two lattices.

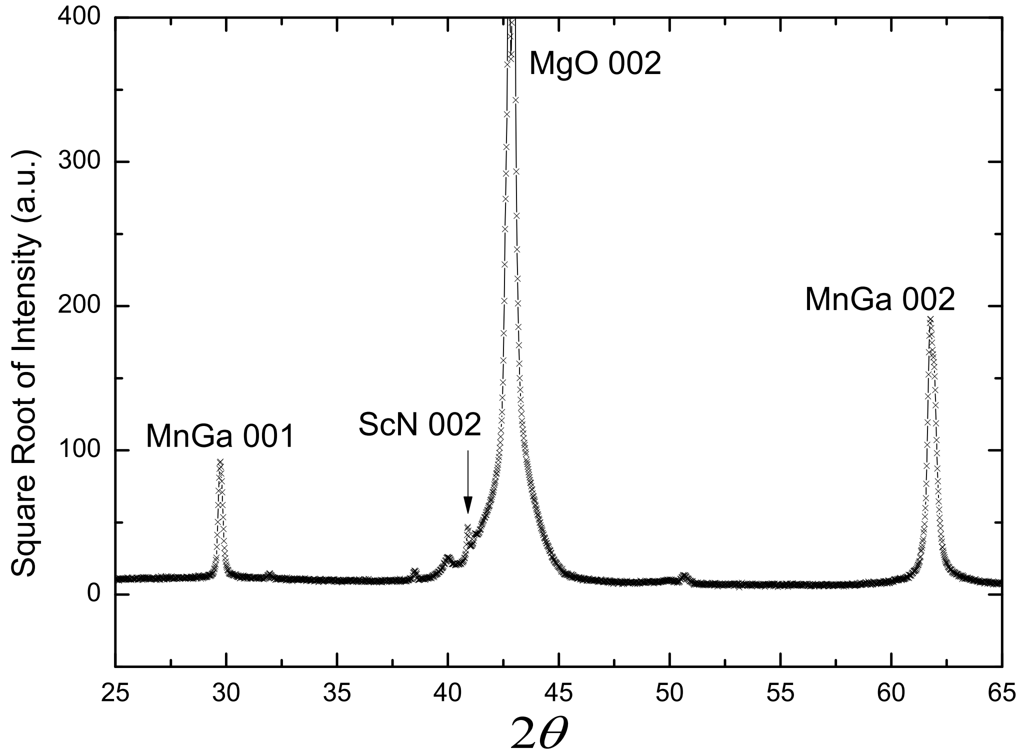

FIG. 3: θ to 2θ X-ray diffraction spectrum acquired on δ-MnGa film grown on ScN/MgO(001).

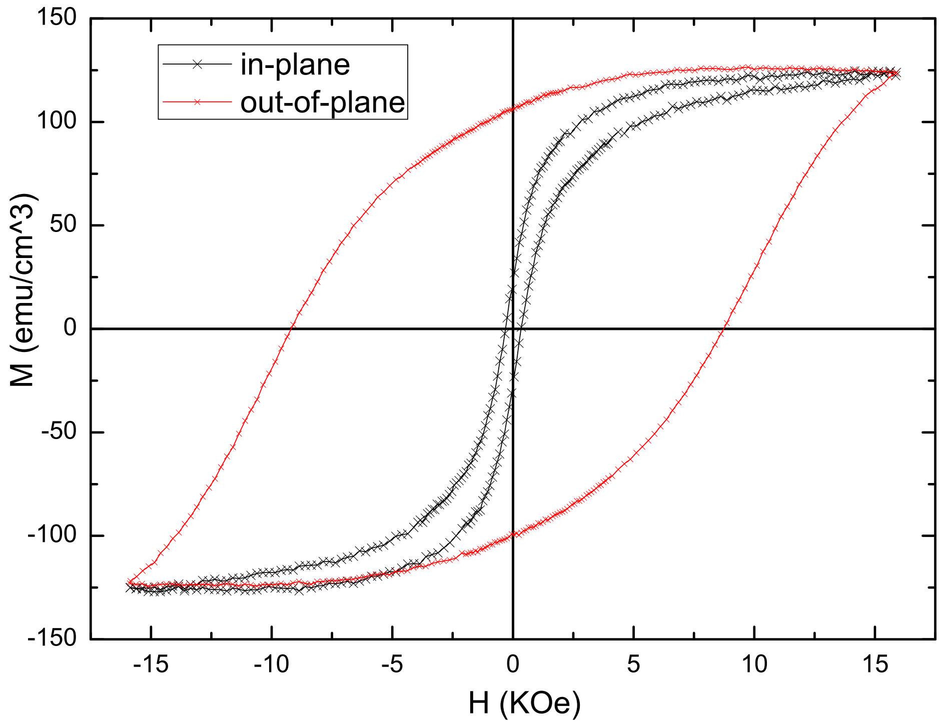

FIG. 4: Magnetization as a function of applied magnetic field with the field applied parallel and perpendicular to the δ-Mn_3Ga_2(001) film surface. Measurements were made with vibrational sample magnetometry at room temperature(27 $^\circ C$).