

Magnetic properties of MBE grown Mn_4N on MgO , SiC , GaN and Al_2O_3 substrates ^F

Cite as: AIP Advances **10**, 015238 (2020); <https://doi.org/10.1063/1.5130485>

Submitted: 23 October 2019 . Accepted: 19 December 2019 . Published Online: 23 January 2020

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Presented: 7 November 2019 • Submitted: 23 October 2019 •

Accepted: 19 December 2019 • Published Online: 23 January 2020



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Note: This paper was presented at the 64th Annual Conference on Magnetism and Magnetic Materials.

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ABSTRACT

Mn_4N is a compound magnetic material that can be grown using MBE while exhibiting several desirable magnetic properties such as strong perpendicular magnetic anisotropy, low saturation magnetization, large domain size, and record high domain wall velocities. In addition to its potential for spintronic applications exploiting spin orbit torque with epitaxial topological insulator/ferromagnet bilayers, the possibility of integrating Mn_4N seamlessly with the wide bandgap semiconductors GaN and SiC provides a pathway to merge logic, memory and communication components. We report a comparative study of MBE grown Mn_4N thin films on four crystalline substrates: cubic MgO , and hexagonal GaN , SiC and sapphire. Under similar growth conditions, the Mn_4N film is found to grow single crystalline on MgO and SiC , polycrystalline on GaN , and amorphous on sapphire. The magnetic properties vary on the substrates and correlate to the structural properties. Interestingly, the field dependent anomalous Hall resistance of Mn_4N on GaN shows different behavior from other substrates such as a flipped sign of the anomalous Hall resistance.

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I. INTRODUCTION

Epitaxial growth of ferromagnets by molecular beam epitaxy (MBE) is of high technical interest for spintronic applications such as devices exploiting spin orbit torque (SOT). Recently, spin orbit switching in MBE grown ferromagnet/topological insulator bilayers with a critical current as low as 1.5 MA/cm^2 has been demonstrated.¹ Mn_4N , which is a room temperature ferrimagnet, has been successfully grown by MBE by a few groups.^{2–5} These MBE grown Mn_4N films show strong perpendicular magnetic anisotropy ($K_u = 1.1 \times 10^5 \text{ J/m}^3$), low saturation magnetization ($M_s = 6.6 \times 10^4 \text{ A/m}$),⁶ large domain size (\sim millimeter size on STO),⁵ and record high domain wall velocities driven by spin transfer torque (up to 900 m/s).⁶ This makes Mn_4N attractive for spintronic devices. Meanwhile, the

successful growth of Mn_4N on SiC ⁴ indicates a strong potential for the seamless integration of Mn_4N with wide bandgap semiconductors of the hexagonal crystal family such as SiC , GaN , AlN , and Sapphire. Such integration may bring spintronic functionality into the burgeoning electronics and photonics applications that these wide-bandgap semiconductor platforms are enabling today.⁷

Most reports on the epitaxial growth of Mn_4N are on oxide substrates such as MgO and SrTiO_3 (STO). Detailed study of the magnetotransport properties such as the anomalous Hall effect of MBE Mn_4N films grown on other substrates are still lacking. In this work, we report the successful MBE growth of Mn_4N films on four substrates: cubic MgO , and wide bandgap semiconductors (SiC and GaN) and sapphire, the last three of which are hexagonal. A comparative study of the crystalline, structural, electronic, magnetic, and

magnetotransport properties of the Mn_4N epitaxial films on the four substrates is conducted.

II. GROWTH AND CHARACTERIZATION METHODS

The Mn_4N layers were grown by plasma assisted MBE in a Veeco GEN II system. All Mn_4N films were grown directly on the substrates without any homoepitaxial buffer layer. The growths on all 4 substrates were performed at a thermocouple temperature of 700°C (unless stated otherwise) for one hour. The growth was monitored by *in situ* reflection-energy electron diffraction (RHEED). A detailed description of sample preparation and characterization methods are provided in the supplementary section.

III. RESULTS AND DISCUSSIONS

A. Crystal quality

Manganese nitride is known to crystallize in several bulk phases such as MnN , Mn_3N_2 , Mn_2N_x and Mn_4N . Among them, only Mn_4N is ferrimagnetic.⁸ As shown in inset of Fig. 1(a), Mn_4N has an antiperovskite crystal structure with a nitrogen (N) atom located at the body center, and two inequivalent manganese sites (Mn_A and Mn_B) with magnetic moments of $3.85 \mu_B/\text{f.u.}$ and $0.9 \mu_B/\text{f.u.}$ occupying the corner and face-centered positions,⁹ respectively. The crystal structure of Mn_4N belongs to the space group $P43_2m$, with the $\{111\}$ planes of Mn_4N exhibiting trigonal symmetry. Fig. 1(a) shows the energy bandgap and lattice constants of the four substrates chosen in this work. The expected epitaxial relationship of Mn_4N with the substrates are Mn_4N (001)// MgO (001) and Mn_4N (111)// GaN (SiC and sapphire) (0001), as is shown in Fig. 1(b). Among these substrates, Mn_4N is most lattice and symmetry matched to MgO . The lattice mismatch with sapphire is as high as 74.6%.

Growth of Mn_4N directly on MgO initiates with a very short nucleation process with spotty RHEED pattern, and gradually changes to bright, streaky pattern as shown in Fig. 2(a) in less than one minute. This indicates a smooth surface, and single crystallinity of the Mn_4N film. The corresponding X-Ray Diffraction (XRD) spectrum shown in Fig. S1(a) corroborates that the Mn_4N grown on MgO is single crystal with the 001 orientations out of plane. The additional peak at 40.4° might be due to the inclusion of pure Mn or formation of MnO because of oxidation, which has been

reported in previous works.^{9,10} The surface is very smooth with root mean square (rms) of 8 angstrom as seen in Fig. S2(a). The structural properties of Mn_4N grown on MgO are therefore excellent, in line with earlier reports, and its magnetotransport properties are discussed later in a comparative fashion with those grown on the other substrates.

When Mn_4N is directly grown on GaN , the initial RHEED forms a bright spotty pattern shown in Fig. 2(b). Pairs of symmetric spots on either side of the original first order streaks of Mn_4N are observed. This RHEED pattern implies the existence of twin domains, that are expected since a three-fold symmetric cubic Mn_4N crystal is being grown on a six-fold symmetric hexagonal GaN substrate, similar to a recent observation of the growth of cubic ScN on GaN .¹¹ The RHEED pattern gradually becomes dimmer, and develops into a polycrystalline ring by the end of the one-hour growth as shown in Fig. 2(c). The Mn_4N thin film deposited directly on GaN is found to be polycrystalline (Fig. S1(b)), evidenced by both (111) and (002) peaks of the crystal. XRD peaks from Al_2O_3 and AlN originate from GaN (on sapphire) templates which were used as substrates for growths in this study.

A strong dependence of the resulting manganese nitride phases on the growth temperature is observed. A secondary phase of $\text{Mn}_2\text{N}_{0.86}$ is found to form as evidenced by the XRD peak marked with arrow in the inset of Fig. S1(c), when grown at 600°C directly on GaN substrates. A possible reason is the thermal stability of the manganese nitride compounds: Mn_4N is the thermally stable phase at higher temperature than $\text{Mn}_2\text{N}_{0.86}$.⁸ The resulting Mn_4N is rather rough, with a surface rms of 34 nm for a 10×10 micron² scan as shown in Fig. S2(b).

For the growth on SiC, the initial RHEED shows a similar spotty pattern during nucleation as seen on GaN (Fig. 2(d)). As can be seen in Fig. S1(d), the epitaxial Mn_4N on SiC is a single-phase crystal with twinning, showing only the (111) XRD peak, as expected from the symmetry of substrates. The surface morphology is quite rough, characterized by a rms of 38 nm for a 10×10 micron² scan as seen in Fig. S2(c). The XRD spectra of single crystalline Mn_4N is consistent with the spotty RHEED pattern maintained throughout the growth, unlike on the GaN substrate where it becomes polycrystalline.

The MBE growth of Mn_4N on SiC and GaN with a presumably smoother surface has been reported in Ref. 4. At this stage, we are unable to explain the difference in surface morphology observed earlier and this study. The possible reasons could be different surface treatments or nucleation conditions before growth, or the major difference could stem from the fact that the instead of the plasma source for nitrogen used here, the MBE growths in the previous study was performed using a NH_3 source.⁴

When grown directly on sapphire, the RHEED pattern of manganese nitride develops into very dim and diffusive pattern less than five minutes into the growth. No peaks other than from substrate are seen in the XRD spectrum for the film grown on sapphire, indicating an amorphous nature of the film. From the magnetic characterization shown latter, ferromagnetism is still observed, likely due to nanocrystalline Mn_4N , the only ferromagnetic phase of manganese nitride at room temperature. The surface morphology is rough with a rms of 66 nm for a 10×10 micron² scan as shown in Fig. S2(d). Since the surface of sapphire was not nitridized prior to the deposition, this is likely due to the large lattice mismatch between Mn_4N and sapphire.

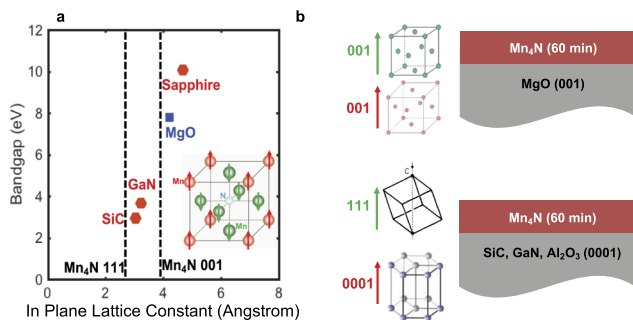


FIG. 1. (a) Bandgap and lattice constant of different substrates (inset) Crystal structure of Mn_4N (b) Schematic of MBE growth of Mn_4N on different substrates.

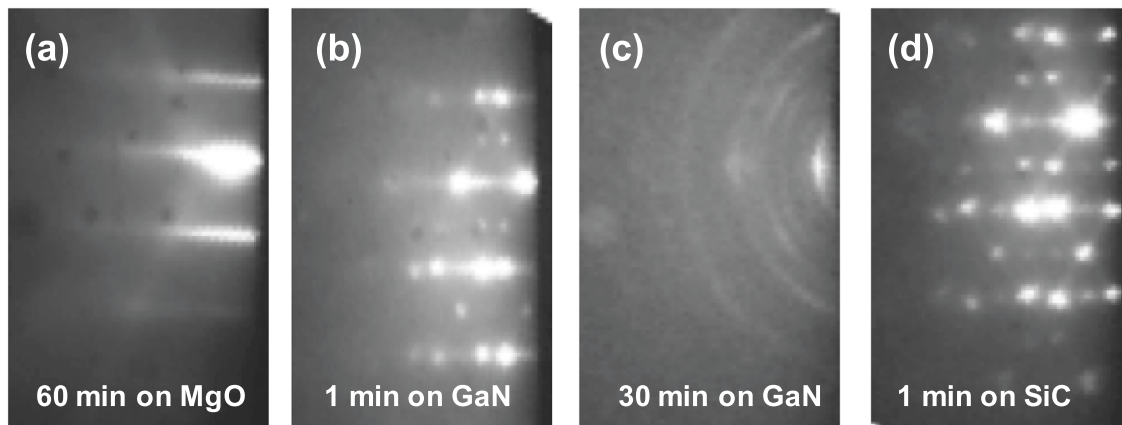


FIG. 2. RHEED images (a) 60 min into Mn_4N growth on MgO (b) 1 min into growth on GaN (c) 30 min into Mn_4N growth on GaN (d) 1 min into Mn_4N growth on SiC.

Therefore, Mn_4N grows single crystalline on MgO with smooth surface. On GaN, the Mn_4N film is rough and polycrystalline, with both (002) and (111) orientations out of plane. It is single crystalline on SiC, though the surface is rough. On sapphire, the film is very rough and amorphous. Table S1 summarizes the crystalline qualities of Mn_4N films deposited directly on these substrates without nucleation layers.

B. Magnetic properties

The film grown on MgO exhibits a square hysteresis loop with almost full remanence at zero field (Fig. 3 (a)). The sharp switching of the magnetization for this sample and comparison with in plane M vs H loop (Fig. S3 (a)) indicate a strong perpendicular magnetic anisotropy (PMA).

The out of plane M vs H loop of Mn_4N on GaN shown in Fig. 3(b) is significantly different from that grown on SiC (Fig. 3(c)). Considering the similarity between SiC and GaN, this sharp contrast

in magnetic properties is quite surprising. Though the saturation magnetization on GaN at 5 K is similar to Mn_4N on SiC, the saturation magnetization drops significantly towards 300 K, reaching only about 50 emu/cc. A similar large drop of the saturation magnetization of Mn_4N with increase in temperature was also reported in Mn_4N grown on $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT) substrates.¹² It is worth mentioning that magnetic properties of manganese nitride films grown on GaN depend critically on growth temperature, for example there is a large difference in coercive field between the film grown at 700 °C and the film grown at 600 °C with clear evidence of $\text{Mn}_2\text{N}_{0.86}$ inclusion.

The saturation magnetization and coercive field of Mn_4N on SiC seen in Fig. 3(c) are both comparable to an earlier report.⁴ The switching of magnetization is not as sharp as Mn_4N on MgO, possibly due to more structural defects, or weaker PMA on SiC (Fig. S3 (c)). Because strain is believed to be the origin of strong PMA in Mn_4N ,^{9,13} the PMA strength is likely to be weaker on strain-relaxed Mn_4N on SiC.

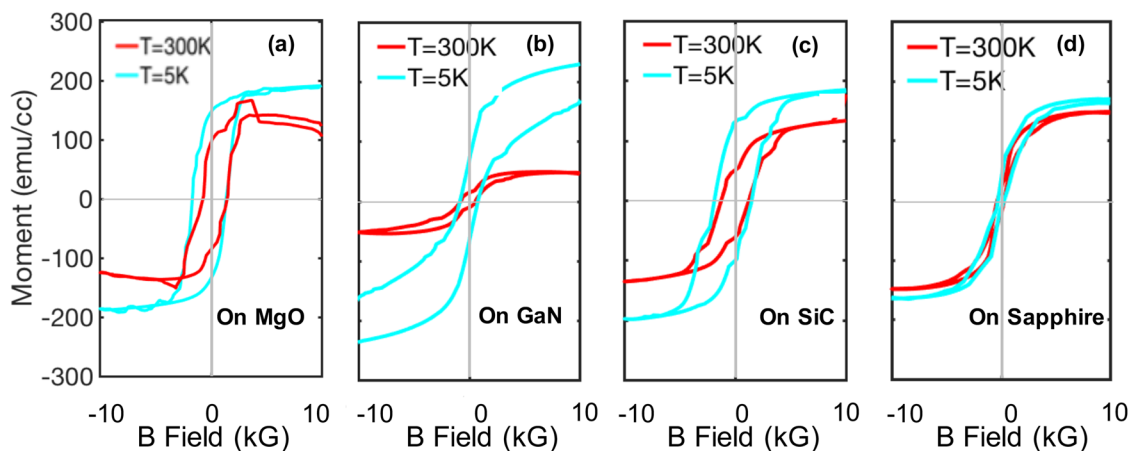


FIG. 3. Out of plane M vs H hysteresis curves at 300 K and 5 K of Mn_4N films grown by MBE on (a) MgO (b) GaN (c) SiC and (d) Sapphire.

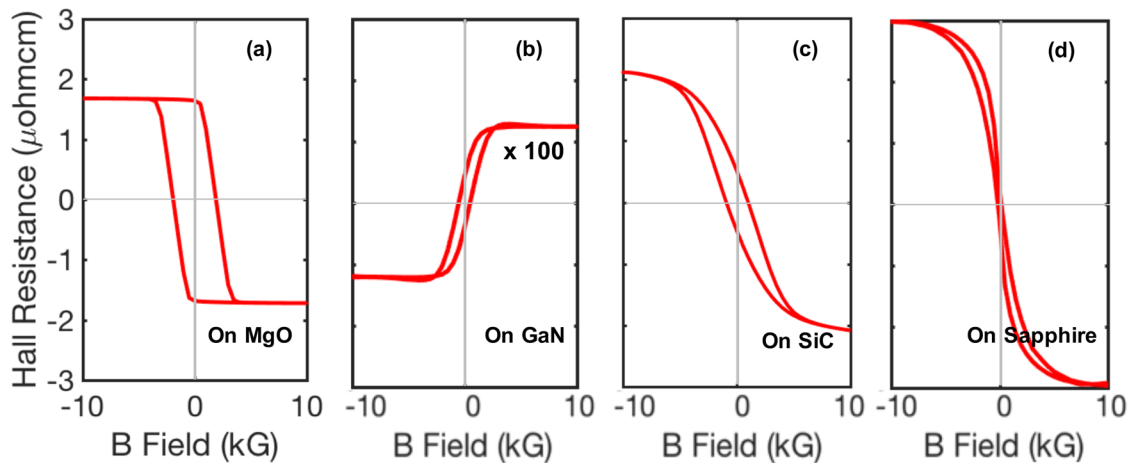


FIG. 4. Anomalous Hall resistance of Mn_4N grown on (a) MgO (b) GaN (c) SiC and (d) Sapphire at 300K.

Though Mn_4N -related XRD peaks were not observed for the film grown on sapphire, Fig. 3(d) nevertheless shows a weak hysteresis loop. Since Mn_4N as the only ferrimagnetic phase at room temperature, it is reasonable to attribute the film grown on sapphire to have Mn_4N inclusions, though the crystal quality is poor, and the surface is rough.

Comparisons between in plane and out of plane M vs H loops of Mn_4N on different substrates are shown Fig. S3. Mn_4N epitaxial layers are found to exhibit PMA on all the four substrates.

The longitudinal resistivity R_{xx} of the Mn_4N epitaxial layer is $143 \mu\Omega \text{ cm}$ on MgO, slightly lower than the reported value of $187 \mu\Omega \text{ cm}$ in Refs. 5 and 6. The longitudinal resistance on GaN is similar to Mn_4N on MgO. However, layers grown on SiC and sapphire are almost twice as resistive, as summarized in Table. S2. Fig. 4 shows that the anomalous Hall resistance of all the films resemble the shape of the M vs H hysteresis curves. However, the Hall resistance is almost two orders smaller for Mn_4N grown on GaN, than on the other substrates [note the different scales in Fig. 4 (b)]. The Hall angle $\theta = R_{xy}/R_{xx}$ is as large as 0.01 for Mn_4N grown on MgO, consistent with earlier reports,^{5,6} while being smaller (0.007 and 0.005) when grown on SiC and sapphire respectively. This is the first report on the magneto transport properties of MBE grown Mn_4N films on substrates other than MgO or STO.

Apart from the extremely small Hall angle (0.002) when grown on GaN, the most interesting feature is the sign reversal of the Hall resistance, seen in Fig. 4 and Fig. S4 (a). Such sign reversal of Hall resistance has been reported in other material system such as epitaxial NiCo (002) films¹⁴ and Co/Pd multilayers.¹⁵ However, in these reports, the sign of the anomalous Hall resistance depends on either the thickness of the layer, the temperature, or the composition ratio of multilayers. These are different from the substrate dependence we observe here. The different strain conditions in Mn_4N films might be a reason, since strain modifies the band structure, resulting in the difference in band filling of Mn_4N films grown on different substrates.¹⁴ However, it is difficult at this stage to explain the difference between films grown on SiC and GaN considering the similar lattice constant and symmetry of the substrates. On the other hand,

for manganese nitride grown on GaN at lower temperatures, where clear XRD peaks from $\text{Mn}_2\text{N}_{0.86}$ can be seen (Fig. S1 (c)), n-type like anomalous Hall resistance is observed (not shown), indicating that the spin states of Mn_4N can vary significantly due to exchange interaction with other magnetic inclusions such as $\text{Mn}_2\text{N}_{0.86}$.

The sign reversal of anomalous Hall resistance of Mn_4N film grown on GaN (Fig. S4 (a)) might be a result of the interaction between Mn_4N and other magnetic inclusions, even though these inclusions are not observed in XRD. This is very likely to happen because of the rich magnetic properties of different phases in (gallium) manganese nitride material system, if we also consider the possibility of inter-diffusion between GaN and Mn_4N . Furthermore, the observation of the shift in M vs H hysteresis loop (Fig. S4 (b)) when field cooling to low temperatures to measure the exchange bias further supports the hypothesis of inclusion of other magnetic phases. Future electron microscopy and chemical analysis is necessary to help unravel the surprising behavior observed in the magnetotransport properties of Mn_4N grown on GaN. Table. S2 summarizes the measured magnetic properties of the samples in this study.

IV. CONCLUSIONS

In summary, ferrimagnetic Mn_4N films were grown directly on four substrates: MgO, GaN, SiC and sapphire under identical growth conditions. No secondary phases are identified from XRD. Based on RHEED and XRD, Mn_4N grows single crystalline on MgO and SiC, polycrystalline on GaN, and amorphous on sapphire. The magnetic properties are found to have a strong correlation with the crystal quality. Mn_4N grown on MgO shows the sharpest switching behavior indicating strong PMA and low density of structural defects. On other substrates, the M vs H curves are not as sharp. The anomalous Hall effect shows n-type like behavior when grown on MgO, SiC, and Sapphire. When grown on GaN at a low substrate temperature, the AHE is n-type like behavior, which switches to p-type like behavior when grown at a higher substrate temperature of 700°C . The sign reversal of the anomalous Hall effect, together with the observation of exchange bias indicates possible inclusion of other

magnetic phases in Mn_4N films grown on GaN. To exploit the integration of Mn_4N with wide bandgap semiconductors such as GaN and SiC by MBE, it is essential that methods of nucleation that lead to much smoother surface morphologies be developed soon. Then, the rich magnetic properties that can already be observed in the current samples can be improved significantly, and the use of epitaxially integrated magnets can enable new applications that take advantage of the wide bandgap semiconductor electronics and photonics platform.

SUPPLEMENTARY MATERIAL

The [supplementary material](#) provides the details of growth and characterization methods, X-Ray Diffraction (XRD) spectra, atomic force microscopy (AFM) images, additional magnetic characterization data and summary of crystal quality and magnetic properties of Mn_4N films deposited on 4 different substrates.

ACKNOWLEDGMENTS

This work was supported in part by the Semiconductor Research Corporation (SRC) as nCORE task 2758.001 and NSF

under the E2CDA program (ECCS 1740286) and NewLAW EFRI 1741694. The project used the Shared Facilities sponsored by the NSF MRSEC program (DMR-1719875, CCMR) and MRI DMR-1338010. The authors would also like to thank Prof. Daniel C. Ralph for helpful discussions.

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