As-grown $\text{Mn}_3\text{CuN}$ thin films with high crystallinity prepared by dynamic aurora pulsed laser deposition

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M$\text{n}_3\text{CuN}$ thin films were prepared using dynamic aurora pulsed laser deposition (PLD), which enables magnetic field application during film growth. The magnetic field can stabilize a plasma state of nitrogen in plume generated from a nitride target. Results show that M$\text{n}_3\text{CuN}$ phase with high crystallinity is observed clearly and grown epitaxially on MgO(001) in the as-grown thin films. The as-grown thin films show ferromagnetic transition near 150 K without post-annealing, indicating almost no nitrogen deficiency. These results suggest that dynamic aurora PLD is effective for nitride thin films with high crystallinity.

Key-words : Antiperovskite, Nitride, Epitaxial thin film, PLD, Nitrogen plasma

1. Introduction

Antiperovskite Mn-based nitrides M$\text{n}_x\text{A}_y\text{N}$ ($A$: metal or semiconducting element) have attracted attention because of their various functional properties such as magnetovolume effect,$^{1,2}$ giant magnetostriiction,$^{3,4}$ low temperature coefficient of resistance (TCR),$^{5,6}$ anomalous perpendicular magnetic anisotropy,$^{7,8}$ high spin-polarization,$^{9}$ and spin-glass behavior.$^{10}$ Although antiferromagnetic transition occurs in most M$\text{n}_x\text{A}_y\text{N}$ family materials ($A = \text{Ni, Zn, Ga, Ag, etc.}$),$^{1,13}$ M$\text{n}_3\text{CuN}$ shows ferromagnetic transition at 143 K with structural transition to tetragonal.$^{3,4}$ It is particularly interesting that giant magnetostriiction up to 2000 ppm, which is comparable to Tb$_2\text{Dy}_{1-x}\text{Fe}_2$ (Terfenol-D),$^{1,4}$ has been reported in a M$\text{n}_3\text{CuN}$ bulk sample below the Curie temperature ($T_C$) and that low TCR is also observed near 300 K. Reportedly, martensitic transformation is the key mechanism for the giant magnetostriiction,$^{3,4}$ but the related details remain unclear. Fundamental studies generally require single crystals. Aoki et al. reported the preparation of M$\text{n}_3\text{GaN}$ using Na flux method, but the method required high pressure of nitrogen (5 MPa). Moreover, the M$\text{n}_3\text{GaN}$ single crystals were small (approx. 200 nm).$^{15}$ For evaluation methods such as photoemission spectroscopy, single-crystal-like specimen with wide area (>1 mm$^2$) is preferable. It can be achieved easily in epitaxial thin films with high crystallinity. In addition, M$\text{n}_3\text{CuN}$ thin films are important for device applications such as micro-actuators and standard resistors.$^{3,4,6}$

The preparation of M$\text{n}_3\text{CuN}$ thin films has already been reported using several methods with the supply of nitrogen plasma because film nitration is difficult to achieve merely by introducing nitrogen gas as a result of the low reactivity. Na et al. reported the preparation of M$\text{n}_3\text{CuN}$ on Si(001) substrates by facing target magnetron sputtering.$^{16}$ Aoyama et al. adopted ultrahigh-field sputtering for the preparation of M$\text{n}_3\text{CuN}$ thin films on MgO(001) substrates.$^{17}$ Their as-grown thin films were single-phased and [001]-oriented out-of-plane. The ferromagnetic transition, however, exhibited higher temperature of stoichiometric bulk sample. The temperature dependence of resistivity showed no anomaly corresponding to magnetic and/or structural transition. The results indicate that the crystalline quality was less and/or the N site of M$\text{n}_3\text{CuN}$ was deficient because nitrogen deficiency increases the $T_C$ to higher temperature reported in bulk M$\text{n}_3\text{CuN}$ samples.$^{3,4,6}$ Recently, the crystallinity of M$\text{n}_3\text{CuN}$ thin films grown using ultrahigh field sputtering has been improved by post-annealing in an evacuated quartz tube with titanium powder, resulting in the shift of $T_C$ to about 150 K.$^{18}$ Post-annealing at high temperature, however, is not preferable to device application because of expectations from the preparation of as-grown M$\text{n}_3\text{CuN}$ thin films with high crystallinity. For obtaining thin films with high crystallinity, pulsed laser deposition (PLD) and molecular beam epitaxy (MBE) are generally more suitable than sputtering method because of vacuum used during thin film growth.

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Plasma-assisted MBE and PLD have been developed and adopted for the preparation of antiperovskite nitride and perovskite oxynitride thin films.\(^{19-21}\) For a Mn–Cu–N system, Mn\(_3\)CuN thin films have been obtained by plasma-assisted MBE.\(^{19}\) The thin films were neither single-orientation nor single-phased, but the crystalline quality was high. The nitrogen plasma source is effective because of the high reactivity, but an increase of background pressure is unavoidable, possibly resulting in the decrease of surface migration of ad-atoms on substrates and thin films.

Recently, we developed dynamic aurora PLD, for which a magnetic field is applied during thin film growth using an electromagnet inside a vacuum chamber.\(^{22-25}\) The applied magnetic field suppresses the adiabatic expansion and the recombination of ions and electrons in the plume, which increases the growth rate, lowers the crystallization temperature, improves film crystallinity, and promotes spinodal decomposition.\(^{23}\) This study shows that a nitride target in dynamic aurora PLD can function as a plasma source of nitrogen. In conventional PLD, nitrogen plasma can be generated by laser ablation, but it is recombined to a neutral state before reaching a substrate because of the high reactivity, but an increase of back-scattering. This would contain positively charged nitrogen radicals, which increases the growth rate, lowers the crystallization and the recombination of ions and electrons in the plume, resulting in the re-excitation enhancement of particles in a neutral state to a plasma state. With dynamic aurora PLD, therefore, the nitrogen plasma in the plume can maintain its plasma state until reaching the substrate by the suppression of plasma recombination by application of the magnetic field. Therefore, nitrogen plasma can be supplied by magnetic field application without introducing a plasma source, as plasma-assisted methods. Because of no introduction of gas flow from a plasma source, a higher vacuum state can also be realized during thin film growth using dynamic aurora PLD. Thus, for this study, we adopted dynamic aurora PLD for thin film growth of Mn\(_3\)CuN. Results show that as-grown Mn\(_3\)CuN epitaxial thin films with high crystallinity were grown on MgO(001) substrates at 500 °C using dynamic aurora PLD. Although MnO and Cu phases are also detected in addition to Mn\(_3\)CuN phase for all thin films grown with an applied magnetic field, not only Mn\(_3\)CuN but also MnO and Cu phases are grown epitaxially on MgO(001) substrate with lattice relaxation. The thin films clearly show ferromagnetic transition near 150 K, which is similar to that of a stoichiometric Mn\(_3\)CuN bulk sample.

2. Experimental procedure

Using dynamic aurora PLD, Mn\(_3\)CuN thin films were grown on MgO(001) substrates. For this study, additional nitrogen gas was not flowed. Thereby, we were able to confirm whether nitrogen in the plume generated from a nitride target was effective for thin film nitration. The only nitrogen source is a nitride target used for that purpose. The nitrogen amount in the target is expected to be more than a synthesized Mn\(_3\)CuN target (N/Cu approx. 1) for sufficient nitridation of thin films. Therefore, as a target, Mn\(_2\)N\(_{1-x}\) powder (99.9%, 200 mesh) and Cu fine powder (99.99%, ca. 1 μm) with the ratio of Mn/Cu = 3 were mixed and sintered in a carbon crucible by spark-plasma-sintering (SPS) process at 300 °C and 30 MPa for 2 min. In the sintered pellet, no additional diffusion peak except for starting materials was confirmed in the X-ray diffraction (XRD) pattern, which implies that no reaction occurred between Mn\(_2\)N\(_{1-x}\) and Cu in the SPS target. Therefore, the nitrogen content in the target did not change from the starting composition (N/Cu > 1). The MgO substrate was cleaned thermally at 800 °C for 30 min before growth for eliminating a native hydroxide surface layer on MgO. It is noteworthy that no Mn\(_3\)CuN peak was found in XRD without this thermal cleaning, even in the optimal growth condition. Subsequently, the substrate temperature was set to 500 °C as the growth temperature. Then a magnetic field (B\(_g\)) was applied during growth using an electromagnet installed in the growth chamber. The pulsed laser was focused and irradiated to the Mn\(_2\)N + Cu target with fluence of 2.0 J/cm\(^2\) and frequency of 10 Hz. The background vacuum pressure during thin film growth was 1 × 10\(^{-6}\) Torr in this study because no load-locked chamber was equipped in the dynamic aurora PLD system. It is noteworthy that no gas including nitrogen was introduced into the chamber during growth. All thin film thicknesses were 100–150 nm with controlling the growth time because the growth rate increases with B\(_g\).\(^{23}\)

The crystalline structure of obtained thin films was evaluated using Cu-Kα XRD (Advance D8; Bruker Ltd.) for 2θ scans and ATX-G (Rigaku Corp.) for other XRD measurements. In ATX-G, the Cu-Kα\(_1\) line was used by selecting the channel monochromator. The film thickness was confirmed by combination with the cross-sectional view measured using scanning electron microscopy (JSM-7001F; JEOL Ltd.). The peak intensity of wavelength dispersive spectra was measured using an electron-probe micro-analyzer (EPMA, JXA-8530F; JEOL Ltd.). Using the EPMA, we also confirmed the thin film composition. All thin film compositions obtained in this study had a Mn/Cu ratio in the range of 2.8–3.1. X-ray photoemission spectroscopy (XPS) was conducted (ESCA-3400; Shimadzu Corp.). In the XPS chamber, the thin film surface was etched using Ar\(^+\) ion milling for eliminating adsorbed molecules on the thin film surface and possibly the oxidized surface layer. The magnetization was measured (MPMS-XL7; Quantum Design) with application of a 100 Oe magnetic field for the direction parallel to in-plane of the thin films.

3. Results and discussion

Figure 1 shows XRD patterns of thin films grown on MgO under various B\(_g\) and a raw MgO substrate. Except for substrate peaks, three peaks are confirmed clearly around 2θ = 40.3–40.7, 46.8, and 49.8–50.1° in Fig. 1.
The three XRD peaks likely correspond respectively to the (002) peak of MnO with \( \alpha = 0.4446 \) nm (Fm-3m (No. 225), ICSD-9864), the (002) peak of Mn\(_3\)CuN with \( \alpha = 0.3906 \) nm (Pm-3m (No. 221), ICSD-628356), and the (002) peak of Cu with \( \alpha = 0.3615 \) nm (Fm-3m (No. 225), ICSD-43493). Under \( B_g = 0 \) G, as with the conventional PLD method, no peak related to Mn\(_3\)CuN phase is observed, although MnO(002) peak and tiny Cu(002) peak are observed. Actually, the thin film shows insulation and half transparency with brown. The oxide phase formation results from residual oxygen remaining in the chamber with poor background vacuum pressure (1 \( \times \) 10\(^{-6} \) Torr) and the oxide contamination in the Mn\(_2\)N–Cu target as shown in Fig. S1 (support information). However, the Mn\(_3\)CuN(002) peak is observed clearly in thin films grown under \( B_g \geq 200 \) G in addition to MnO and Cu peaks. As shown in the inset of Fig. 1, all thin films grown under \( B_g \geq 200 \) G have a mirror-like black surface, which implies a metallic property, as reported for bulk Mn\(_3\)CuN samples.

Figure 2 shows XPS spectra of the thin film grown under 2000 G. The clear observation of oxygen existence in the thin film [Fig. 2(d)] supports our inference that the XRD peak around 40.5° shown in Fig. 1 stems from MnO. The nitrogen peak is also observed clearly in Fig. 2(c), indicating coexistence of nitride. The peak energies in the three spectra for Mn 2p, Cu 2p, and N 1s core levels [Figs. 2(a)–2(c)] are closely consistent with the XPS spectra reported for a Mn\(_{1.6}\)Cu\(_{0.4}\)N thin film grown using plasma MBE,\(^{19}\) indicating that the thin film grown under 2000 G includes antiperovskite Mn\(_3\)CuN phase. The coexistence of Mn\(_3\)CuN and metal Cu phase, as presented in Fig. 1, is likely explained by the fact that satellite peaks of Cu 2p at around 945 and 965 eV [Fig. 2(b)], indicating the existence of divalent Cu, are weaker than those reported for Mn\(_{1.6}\)Cu\(_{0.4}\)N thin film grown using plasma MBE.\(^{19}\) As described above, the only nitrogen source in this study is the nitride target because no additional nitrogen gas was introduced into the growth chamber. Furthermore, no Mn\(_3\)CuN phase is observed in thin films grown under \( B_g = 0 \) G. These results indicate that the nitrogen plasma, as expected, is supplied from the nitride target because of suppression of plume recombination by application of the magnetic field during growth. Therefore, dynamic aurora PLD is demonstrated as an effective method for nitride thin film growth.

Figure 3 presents XRD analyses of crystallinity of the Mn\(_3\)CuN phase in the thin films obtained in this study. For

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Figure 3 presents XRD analyses of crystallinity of the Mn\(_3\)CuN phase in the thin films obtained in this study. For
the thin film grown under 1000 G, the full width at half maximum (FWHM) values of the Mn$_3$CuN(002) peak in the $\omega$ rocking curve, $\Delta\omega_{002}$, is 1.15° [Fig. 3(a)]. Four-fold symmetric peaks are observed clearly in the in-plane $\phi$ scan of Mn$_3$CuN(111) peaks as shown in Fig. 3(b). These profiles indicate that the Mn$_3$CuN phase is grown epitaxially on the MgO(001) substrate. Furthermore, the FWHM value of (111) peak in $\phi$ scan, $\Delta\phi_{111}$, is 1.52°, which is sharper than the reported value of as-grown Mn$_2$CuN thin film created using ultrahigh-field sputtering method (about 3.2°) and comparable to the post-annealed thin film (1.143°). Moreover, as depicted in Fig. 3(c), both $\Delta\omega_{002}$ and $\Delta\phi_{111}$ become sharper with increasing growth magnetic field $B_g$, indicating that applying a magnetic field during PLD growth assists the improvement of crystallinity. As reported from earlier studies, an increase of ion flux impingement by suppressing plasma recombination because of applying magnetic field decreases the activation energy of diffusion in thin films. This result leads to improvement of atomic migration and the crystalline rearrangement at nearby surfaces: as-grown thin film by dynamic aurora PLD can achieve high crystallinity without post-annealing.

**Figure 4** shows reciprocal space mapping (RSM) of the thin film grown under 1000 G. In addition to the (113) spot of the MgO substrate, three spots of MnO(113), Mn$_3$CuN(113), and Cu(113) are observed in the RSM. Surprisingly, the (113) diffraction of all phases was observed as “spot”, indicating that all phases are grown epitaxially on MgO(001) substrate in a cube-on-cube manner. Considered along with the spot positions in RSM, the in-plane lattice parameters of all phases in the thin film have the same out-of-plane lattice parameters, which means that their lattices are relaxed. Because the three phases are distributed randomly in thin film as shown in Fig. S2 (support information), they would be grown epitaxially not only on MgO but also on each other such as Mn$_3$CuN/MnO, Mn$_3$CuN/MnO, and Cu/Mn$_3$CuN. The lattice relaxations of all phases also support the epitaxial growth on one another because of the large mismatches between MgO and other phases. The epitaxial growth on one another is probably the reason why the crystallinity of Mn$_3$CuN phase is high in spite of the coexistence of MnO and Cu phases in the thin films.

**Figure 5(a)** shows the temperature dependence of magnetization at 20 K ($M_{20K}$) of the thin films under various $B_g$ measured by field cooling. The magnetic field of 100 Oe applied for magnetization measurement was applied parallel to the film surface. (b) The magnetization at 20 K shown in (a) as a function of XRD intensity ratio of [Mn$_3$CuN(002)]/[Mn$_3$CuN(002)] + [MnO(002)]. The broken line is a guide to the eyes.
phase are almost independent of $B_g$, which indicates that the composition of Mn$_3$CuN phase is common for all thin films obtained in this study. The lattice parameter is slightly smaller than that reported for the Mn$_3$CuN bulk sample ($a = 0.3906$ nm; ICSD-628356) in spite of showing $T_C$ of nearly 150 K. This is true, probably because of little lattice distortion by in-plane tensile strain from MgO substrate. Therefore, the Mn$_3$CuN phase in the thin films of this study is the same as the stoichiometric bulk sample, Mn$_3$CuN $= 3:1:1$, with almost no nitrogen deficiency irrespective of the coexistence of MnO and Cu phases. Although $T_C$ is almost independent of $B_g$, magnetization at low temperatures depends on $B_g$. For comparing magnetization at 20 K ($M_{20K}$), the value increases to $B_g = 1000$ G, but it tends to decrease at values greater than 1000 G. In Fig. 1, the MnO(002) peak is higher than that of the Mn$_3$CuN(002) phase in the thin film grown under 2000 G. The magnetization presented in Fig. 5 is calculated using the whole volume of the thin film. The Mn$_3$CuN phase volume fraction in thin film is not considered. Consequently, the $M_{20K}$ value is likely to depend on the volume fraction of Mn$_3$CuN phase in thin film. The reasons for MnO phase formation probably include the decomposition of Mn$_3$CuN and oxidation to MnO. During dynamic aurora PLD with a high magnetic field, ion impingement possibly introduces damage to the thin film; moreover, residual oxygen in the growth chamber and from the oxide contamination in the target can be excited to the oxygen plasma by high-density plasma.\(^{22-25}\)

In the simple assumption, the independent volume fraction of Mn$_3$CuN phase is estimated roughly by comparing XRD peak intensities of the two main phases, MnO and Mn$_3$CuN: [Mn$_3$CuN(002) peak intensity]/([MnO(002) peak intensity] $+ [Mn_3$CuN(002) peak intensity]). As shown in Fig. 5(b), all values of the magnetization at 20 K of the obtained thin films are on one straight line as a function of the intensity ratio of XRD peaks presented in Fig. 1, which supports our inference that the $M_{20K}$ dependence on $B_g$ is determined by the volume fraction of Mn$_3$CuN phase. It is noted that the increase of the Mn$_3$CuN volume fraction dependent on $B_g$ can explain the improvement of the crystallinity of Cu phase in $B_g = 1000$ G observed in Fig. 1 in the assumption of the epitaxial growth on each phase in thin film, as shown in Fig. S3 (support information). The extrapolation of $M_{20K}$ to the Mn$_3$CuN volume fraction of 1 in Fig. 5(b) is greater than 50 emu/cm$^3$, which corresponds to over 0.1 $\mu_B$/Mn with the use of Mn$_3$CuN lattice parameter obtained in this study. Considered with the measurement magnetic field of 100 Oe for Fig. 5, 0.1 $\mu_B$/Mn for Mn$_3$CuN phase in the thin film obtained in this study is reasonable because the reported Mn$_3$CuN thin film grown on MgAl$_2$O$_4$ substrate with post-annealing showed 0.45 $\mu_B$/Mn under the measurement magnetic field of 500 Oe.\(^{18}\)

As described in Table S1 (support information), the volume fraction of Mn$_3$CuN phase estimated using the extrapolated value is about 70 \% for the thin film grown under 1000 G.

4. Conclusions

In summary, as-grown Mn$_3$CuN epitaxial thin films with high crystallinity were grown on MgO(001) substrates at 500 °C using dynamic aurora PLD. Although Mn$_3$CuN phase was not confirmed under 0 G, which is the same as conventional PLD, it was observed clearly under $B_g \geq 200$ G. This result implies that the plume generated from a nitride target under applying magnetic field likely functions as a nitrogen plasma source. The crystallinity of Mn$_3$CuN phase in as-grown thin films obtained in this study is high and comparable to that of post-annealed thin films.\(^{18}\) Although MnO and Cu phases are also detected in all thin films grown under $B_g \geq 200$ G in addition to Mn$_3$CuN phase, not only Mn$_3$CuN but also MnO and Cu phases are grown epitaxially on MgO(001) substrate with lattice relaxation. All thin films grown under $B_g \geq 200$ G clearly show a ferromagnetic transition near 150 K, indicating that the Mn$_3$CuN phases in the thin films almost share a stoichiometric relation (Mn:Cu:N $= 3:1:1$). This study is the first report of as-grown Mn$_3$CuN thin films with $T_C$ of approximately 150 K. These results suggest dynamic aurora PLD as an effective method for preparing nitride thin films.

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| $B_g$/G | $a_{\text{as-MnCuN}}$/nm | $a_{\text{in-MnCuN}}$/nm | $T_C$/K |
|--------|-----------------|-----------------|--------|
| 200    | 0.3882          | 0.390           | 147    |
| 500    | 0.3882          | 0.390           | 147    |
| 1000   | 0.3881          | 0.390           | 147    |
| 1500   | 0.3881          | 0.390           | 144    |
| 2000   | 0.3879          | 0.390           | 151    |
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