FULL PAPER

As-grown Mn_3CuN thin films with high crystallinity prepared by dynamic aurora pulsed laser deposition

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Mn_3CuN 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 Mn_3CuN phase with high crystallinity is observed clearly and grown epitaxially on $\text{MgO}(001)$ 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.

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

[Received November 27, 2020; Accepted March 10, 2021]

1. Introduction

Antiperovskite Mn-based nitrides Mn_3AN (A : metal or semiconducting element) have attracted attention because of their various functional properties such as magneto-volume effect,^{1,2)} giant magnetostriction,³⁻⁵⁾ low temperature coefficient of resistance (TCR),⁶⁻⁸⁾ anomalous perpendicular magnetic anisotropy,^{9,10)} high spin-polarization,¹¹⁾ and spin-glass behavior.¹²⁾ Although antiferromagnetic transition occurs in most Mn_3AN family materials ($A = \text{Ni}$, Zn , Ga , Ag , etc.),^{1,13)} Mn_3CuN shows ferromagnetic transition at 143 K with structural transition to tetragonal.^{3,4)} It is particularly interesting that giant magnetostriction up to 2000 ppm, which is comparable to $\text{Tb}_x\text{Dy}_{1-x}\text{Fe}_2$ (Terfenol-D),¹⁴⁾ has been reported in a Mn_3CuN 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 magnetostriction,^{3,4)} but the related details remain unclear. Fundamental studies generally require single crystals. Aoki et al. reported the preparation of Mn_3GaN using Na flux method, but the method required high pressure of nitrogen (5 MPa). Moreover, the Mn_3GaN single crystals were small (approx. 200 nm).¹⁵⁾ For evaluation methods such as photoemission spectroscopy, single-crystal-like specimen with wide area ($>1 \text{ mm}^2$) is preferable. It can be achieved easily in epi-

taxial thin films with high crystallinity. In addition, Mn_3CuN thin films are important for device applications such as micro-actuators and standard resistors.^{3,4,6)}

The preparation of Mn_3CuN 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 Mn_3CuN on $\text{Si}(001)$ substrates by facing target magnetron sputtering.¹⁶⁾ Aoyama et al. adopted ultrahigh-field sputtering for the preparation of Mn_3CuN thin films on $\text{MgO}(001)$ 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 Mn_3CuN was deficient because nitrogen deficiency increases the T_C to higher temperature reported in bulk $\text{Mn}_3\text{CuN}_{1-x}$ samples.⁴⁾ Recently, the crystallinity of Mn_3CuN 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 Mn_3CuN 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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^{*} Preface for this article: DOI <http://doi.org/10.2109/jcersj2.129.P7-1>

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, $\text{Mn}_{3.6}\text{Cu}_{0.4}\text{N}$ 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, which would contain positively charged nitrogen radicals, can be generated by laser ablation, but it is recombined to a neutral state before reaching a substrate because of the lack of a magnetic field. Under magnetic field, however, the circular motion of charged particles caused by Lorentz force suppresses the collision probability between a positively charged nitrogen and an electron. In addition, the cyclotron motion of charged particles provides the convergence of a 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 plume 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_3CuN . Results show that as-grown Mn_3CuN epitaxial thin films with high crystallinity were grown on $\text{MgO}(001)$ substrates at 500°C using dynamic aurora PLD. Although MnO and Cu phases are also detected in addition to Mn_3CuN phase for all thin films grown with an applied magnetic field, not only Mn_3CuN but also MnO and Cu phases are grown epitaxially on $\text{MgO}(001)$ substrate with lattice relaxation. The thin films clearly show ferromagnetic transition near 150 K, which is similar to that of a stoichiometric Mn_3CuN bulk sample.

2. Experimental procedure

Using dynamic aurora PLD, Mn_3CuN thin films were grown on $\text{MgO}(001)$ 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_3CuN target (N/Cu approx. 1) for sufficient nitridation of thin films. Therefore, as a target, $\text{Mn}_2\text{N}_{1-\delta}$ powder (99.9 %, 200 mesh) and Cu fine powder (99.99 %, ca. $1\ \mu\text{m}$) with the ratio of $\text{Mn}/\text{Cu} = 3$ 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 diffraction peak except for starting materials was confirmed in the X-ray diffraction (XRD) pattern, which implies that no reaction occurred between $\text{Mn}_2\text{N}_{1-\delta}$ and Cu in the SPS target. Therefore, the nitrogen content in the target did not change from the starting composition ($\text{N}/\text{Cu} > 1$). 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_3CuN 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 $\text{Mn}_2\text{N} + \text{Cu}$ target with fluence of $2.0\ \text{J}/\text{cm}^2$ 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 $\text{Cu-K}\alpha$ XRD (Advance D8; Bruker Ltd.) for θ – 2θ scans and ATX-G (Rigaku Corp.) for other XRD measurements. In ATX-G, the $\text{Cu-K}\alpha_1$ 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 $2\theta = 40.3$ – 40.7 , 46.8 , and 49.8 – 50.1° in Fig. 1.

Fig. 1. XRD patterns of obtained thin films on MgO(001) substrates under various applied magnetic fields during growth (B_g). The inset image shows the surface of the thin film grown under 2000 G.

The three XRD peaks likely correspond respectively to the (002) peak of MnO with $a = 0.4446$ nm (Fm-3m (No. 225), ICSD-9864), the (002) peak of Mn_3CuN with $a = 0.3906$ nm (Pm-3m (No. 221), ICSD-628356), and the (002) peak of Cu with $a = 0.3615$ nm (Fm-3m (No. 225), ICSD-43493). Under $B_g = 0$ G, as with the conventional PLD method, no peak related to Mn_3CuN 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 (1×10^{-6} Torr) and the oxide contamination in the Mn_2N -Cu target as shown in Fig. S1 (support information). However, the Mn_3CuN (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_3CuN samples.⁶⁾

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 $\text{Mn}_{3.6}\text{Cu}_{0.4}\text{N}$ thin film grown using plasma MBE,¹⁹⁾ indicating that the thin film grown under 2000 G includes antiperovskite Mn_3CuN phase. The coexistence of Mn_3CuN 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

Fig. 2. XPS of the thin film grown under 2000 G after etching of the surface by Ar^+ ion milling. Spectra are shown around the core level peaks for (a) Mn 2p, (b) Cu 2p, (c) N 1s, and (d) O 1s.

Fig. 3. XRD analyses for the thin film grown under 1000 G: (a) ω rocking curve of Mn_3CuN (002) peak; and (b) ϕ scan of $\text{Mn}_3\text{CuN}\{111\}$ peaks. (c) FWHMs of ω rocking curve of Mn_3CuN (002) peak ($\Delta\omega_{002}$) and ϕ scan of Mn_3CuN (111) peak ($\Delta\phi_{111}$) as a function of B_g .

existence of divalent Cu, are weaker than those reported for $\text{Mn}_{3.6}\text{Cu}_{0.4}\text{N}$ 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_3CuN 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_3CuN phase in the thin films obtained in this study. For

Fig. 4. RSM around (113) spot of MgO substrate in the thin film grown under 1000 G.

the thin film grown under 1000 G, the full width at half maximum (FWHM) values of the $\text{Mn}_3\text{CuN}(002)$ peak in the ω rocking curve, $\Delta\omega_{002}$, is 1.15° [Fig. 3(a)]. Four-fold symmetric peaks are observed clearly in the in-plane ϕ scan of $\text{Mn}_3\text{CuN}\{111\}$ peaks as shown in Fig. 3(b). These profiles indicate that the Mn_3CuN phase is grown epitaxially on the $\text{MgO}(001)$ substrate. Furthermore, the FWHM value of (111) peak in ϕ scan, $\Delta\phi_{111}$, is 1.52° , which is sharper than the reported value of as-grown Mn_3CuN thin film created using ultrahigh-field sputtering method (about 3.2°) and comparable to the post-annealed thin film (1.143°).¹⁸⁾ 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,^{22)–25)} 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 $\text{MnO}(113)$, $\text{Mn}_3\text{CuN}(113)$, and $\text{Cu}(113)$ are observed in the RSM. Surprisingly, the (113) diffraction of all phases was observed as “spot”, indicating that all phases are grown epitaxially on $\text{MgO}(001)$ 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

Fig. 5. (a) Temperature dependence of the 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 $[\text{Mn}_3\text{CuN}(002)]/([\text{Mn}_3\text{CuN}(002)] + [\text{MnO}(002)])$. The broken line is a guide to the eyes.

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 $\text{Mn}_3\text{CuN}/\text{MnO}$, $\text{Mn}_3\text{CuN}/\text{MnO}$, and $\text{Cu}/\text{Mn}_3\text{CuN}$. 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_3CuN 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 of thin films grown under various B_g . For the thin film grown under 0 G, no ferromagnetic transition is observed, which corresponds to no Mn_3CuN phase because MnO exhibits an antiferromagnetic transition below 120 K from paramagnetic influences, and metal Cu shows a diamagnetic property.^{26),27)} However, all thin films grown under $B_g \geq 200$ G clearly show ferromagnetic transition near 150 K, which originates from Mn_3CuN phase because the T_C value is close to that reported for Mn_3CuN bulk samples ($T_C = 143$ K).^{3),4)} As-grown thin films reported by other groups have shown higher T_C than 200 K; post-annealing was needed to reduce T_C to about 150 K. Therefore, this report is the first of a study of as-grown Mn_3CuN thin film with T_C of approximately 150 K. T_C shifts to higher temperatures, as observed with introduction of nitrogen deficiency and increasing Mn/Cu ratio to 4 in $\text{Mn}_3\text{CuN}_{1-x}$ and $\text{Mn}_{3+y}\text{Cu}_{1-y}\text{N}$ bulk samples.²⁸⁾ The out-of-plane and in-plane lattice parameters of Mn_3CuN phase and T_C s of the obtained thin films under various B_g are shown in Table 1. The lattice parameters of Mn_3CuN

Table 1. Out-of-plane and in-plane lattice parameters of Mn_3CuN phase ($a_{\text{out-Mn}_3\text{CuN}}$, $a_{\text{in-Mn}_3\text{CuN}}$) estimated from XRD patterns and T_C determined from Fig. 5(a) of thin films grown under $B_g \geq 200$ G

B_g/G	$a_{\text{out-Mn}_3\text{CuN}}/\text{nm}$	$a_{\text{in-Mn}_3\text{CuN}}/\text{nm}$	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

phase are almost independent of B_g , which indicates that the composition of Mn_3CuN phase is common for all thin films obtained in this study. The lattice parameter is slightly smaller than that reported for the Mn_3CuN 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_3CuN phase in the thin films of this study is the same as the stoichiometric bulk sample, $\text{Mn}:\text{Cu}:\text{N} = 3:1:1$, 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 ($M_{20\text{K}}$), the value increases to $B_g = 1000$ G, but it tends to decrease at values greater than 1000 G. In Fig. 1, the $\text{MnO}(002)$ peak is higher than that of the $\text{Mn}_3\text{CuN}(002)$ 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_3CuN phase volume fraction in thin film is not considered. Consequently, the $M_{20\text{K}}$ value is likely to depend on the volume fraction of Mn_3CuN phase in thin film. The reasons for MnO phase formation probably include the decomposition of Mn_3CuN 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 plume.^{22)–25)} In the simple assumption, the volume fraction of Mn_3CuN phase can be estimated roughly by comparing XRD peak intensities of the two main phases, MnO and Mn_3CuN : $[\text{Mn}_3\text{CuN}(002) \text{ peak intensity}] / ([\text{MnO}(002) \text{ peak intensity}] + [\text{Mn}_3\text{CuN}(002) \text{ peak intensity}])$. 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 $M_{20\text{K}}$ dependence on B_g is determined by the volume fraction of Mn_3CuN phase. It is noted that the increase of the Mn_3CuN 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 $M_{20\text{K}}$ to the Mn_3CuN volume fraction of 1 in Fig. 5(b) is greater than $50 \text{ emu}/\text{cm}^3$, which corre-

sponds to over $0.1 \mu_B/\text{Mn}$ with the use of Mn_3CuN lattice parameter obtained in this study. Considered with the measurement magnetic field of 100 Oe for Fig. 5, $0.1 \mu_B/\text{Mn}$ for Mn_3CuN phase in the thin film obtained in this study is reasonable because the reported Mn_3CuN thin film grown on MgAl_2O_4 substrate with post-annealing showed $0.45 \mu_B/\text{Mn}$ under the measurement magnetic field of 500 Oe.¹⁸⁾ As described in Table S1 (support information), the volume fraction of Mn_3CuN phase estimated using the extrapolated value is about 70 % for the thin film grown under 1000 G.

4. Conclusions

In summary, as-grown Mn_3CuN epitaxial thin films with high crystallinity were grown on $\text{MgO}(001)$ substrates at 500°C using dynamic aurora PLD. Although Mn_3CuN 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_3CuN 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_3CuN phase, not only Mn_3CuN but also MnO and Cu phases are grown epitaxially on $\text{MgO}(001)$ 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_3CuN phases in the thin films almost share a stoichiometric relation ($\text{Mn}:\text{Cu}:\text{N} = 3:1:1$). This study is the first report of as-grown Mn_3CuN thin films with T_C of approximately 150 K. These results suggest dynamic aurora PLD as an effective method for preparing nitride thin films.

Acknowledgements Part of this work was supported by JSPS KAKENHI (Grant-in-Aid for Early-Career Scientists) Grant Number JP20K15173. Part of this work was carried out by the joint usage/research program of the Institute of Materials and Systems for Sustainability (IMaSS), Nagoya University. Part of this work was also carried out under the Cooperative Research Project Program of Research Institute of Electronics, Shizuoka University. Part of this research was also supported by the Collaborative Research Project of Laboratory for Materials and Structures, Institute of Innovative Research, Tokyo Institute of Technology. The SPS process was performed by the help of Professor D. Fu of Shizuoka University.

References

- 1) K. Takenaka, M. Ichigo, T. Hamada, A. Ozawa, T. Shibayama, T. Inagaki and K. Asano, *Sci. Technol. Adv. Mat.*, **15**, 015009 (2014).
- 2) K. Takenaka and H. Takagi, *Appl. Phys. Lett.*, **94**, 131904 (2009).
- 3) T. Shibayama and K. Takenaka, *J. Appl. Phys.*, **109**, 07A928 (2011).
- 4) K. Takenaka, T. Hamada, T. Shibayama and K. Asano,

- J. Alloy. Compd.*, **577S**, S291–S295 (2013).
- 5) T. Shimizu, T. Shibayama, K. Asano and K. Takenaka, *J. Appl. Phys.*, **111**, 07A903 (2012).
- 6) E. O. Chi, W. S. Kim and N. H. Hur, *Solid State Commun.*, **120**, 307–310 (2001).
- 7) T. Oe, C. Urano, N. Kaneko, M. Hadano and K. Takenaka, *Appl. Phys. Lett.*, **103**, 173518 (2013).
- 8) N. P. Lu, T. Xu, Z. X. Cao and A. L. Ji, *J. Phys. D Appl. Phys.*, **49**, 045308 (2016).
- 9) K. M. Ching, W. D. Chang, T. S. Chin, J. G. Duh and H. C. Ku, *J. Appl. Phys.*, **76**, 6582–6584 (1994).
- 10) K. Kabara and M. Tsunoda, *J. Appl. Phys.*, **117**, 17B512 (2015).
- 11) H. Lee, H. Sukegawa, J. Liu, T. Ohkubo, S. Kasai, S. Mitani and K. Hono, *Appl. Phys. Lett.*, **107**, 032403 (2015).
- 12) X. H. Zhang, Q. Yuan, J. C. Han, J. G. Zhao, J. K. Jian, Z. H. Zhang and B. Song, *Appl. Phys. Lett.*, **103**, 022405 (2013).
- 13) D. Fruchart and E. F. Bertaut, *J. Phys. Soc. Jpn.*, **44**, 781–791 (1978).
- 14) A. E. Clark, J. P. Teter and O. D. McMasters, *J. Appl. Phys.*, **63**, 3910–3912 (1988).
- 15) M. Aoki, H. Yamane, M. Shimada and T. Kajiwara, *J. Alloy. Compd.*, **364**, 280–282 (2004).
- 16) Y. Na, C. Wang, Y. Sun, L. Chu, M. Nie, N. Ji and J. Wang, *Mater. Res. Bull.*, **46**, 1022–1027 (2011).
- 17) M. Aoyama, K. Takenaka and H. Ikuta, *J. Alloy. Compd.*, **577S**, S314–S317 (2013).
- 18) T. Matsumoto, T. Hatano, T. Uranta, K. Iida, K. Takenaka and H. Ikuta, *Phys. Rev. B*, **96**, 205153 (2017).
- 19) F. Yu, L. Ren, M. Meng, Y. Wang, M. Yang, S. Wu and S. Li, *J. Appl. Phys.*, **115**, 133911 (2014).
- 20) A. Anzai, F. Takata, T. Gushi, K. Toko and T. Suemasu, *J. Cryst. Growth*, **489**, 20–23 (2018).
- 21) D. Oka, Y. Hirose, H. Kamisaka, T. Fukumura, K. Sasa, S. Ishii, H. Matsuzaki, Y. Sato, Y. Ikuhara and T. Hasegawa, *Sci. Rep.-UK*, **4**, 4987 (2014).
- 22) N. Wakiya, N. Sakamoto, S. Koda, W. Kumasaka, N. Debnath, T. Kawaguchi, T. Kiguchi, K. Shinozaki and H. Suzuki, *NPG Asia Mater.*, **8**, e279 (2016).
- 23) N. Wakiya, T. Kawaguchi, N. Sakamoto, H. Das, K. Shinozaki and H. Suzuki, *J. Ceram. Soc. Jpn.*, **125**, 856–865 (2017).
- 24) N. Debnath, T. Kawaguchi, W. Kumasaka, H. Das, K. Shinozaki, N. Sakamoto, H. Suzuki and N. Wakiya, *J. Magn. Magn. Mater.*, **432**, 391–395 (2017).
- 25) N. Debnath, T. Kawaguchi, H. Das, S. Suzuki, W. Kumasaka, N. Sakamoto, K. Shinozaki, H. Suzuki and N. Wakiya, *Sci. Technol. Adv. Mat.*, **19**, 507–516 (2018).
- 26) C. G. Shull, W. A. Strauser and E. O. Wollan, *Phys. Rev.*, **83**, 333–345 (1951).
- 27) S. R. Rao, *Nature*, **136**, 436 (1935).
- 28) J. Lin, P. Tong, D. Cui, C. Yang, J. Yang, S. Lin, B. Wang, W. Tang, L. Zhang, Y. Zou and Y. Sun, *Sci. Rep.-UK*, **5**, 7933 (2015).