TEM observation of nitrogen-tunable bcc–bct–fcc transformation of iron-cobalt with added vanadium
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Note: This paper was presented at the 64th Annual Conference on Magnetism and Magnetic Materials. 
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ABSTRACT
We used transmission electron microscopy (TEM) to observe tunable bcc–bct–fcc transformation of FeCo films caused by the addition of auxiliary elements. The crystal structure of the FeCo with added V was bcc, and the transformation of the bcc structure through the bct to fcc was found to depend on the N content (x). TEM observation revealed that bct structure with \( c/a = 1.12 \) was obtained for \( x = 1.7 \) atomic\%, while fcc structure with \( c/a = \sqrt{2} \) was obtained for \( x = 9.6 \) atomic\%. The \( c/a \)-values depended on \( x \), so the bcc–bct–fcc transformation of the FeCoV was tunable by N content. This research was made possible by special preventative measures taken during preparation to avoid compressive stress, which could otherwise induce the bct FeCo lattice of axial ratio \( c/a > 1.00 \) to transform to bcc structure. A FeCo coating of thickness 20 nm was therefore deposited directly on a MgO substrate without any other metallic layers.

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I. INTRODUCTION

Due to the recent shift to electric vehicles on a global scale, strong permanent magnets mounted on high performance motors are experiencing strong demand. At present, strong permanent magnets containing rare-earth and/or rare-metal elements such as NdFeB, SmCo, and FePt are mostly used because of their good magnetic properties. The rare-earth magnets are especially valued for their strong magnetic anisotropy due to the 4f orbital, while the heavy rare-metal magnets are especially valued for the large magnitude of their spin-orbit interaction. However, these magnets are extremely expensive and are supplied by a limited production area.\textsuperscript{1,2} Development of strong permanent magnets free of rare-earth and rare-metal elements constitutes one of the most efficient ways to solve the problem of magnet demand, since less exotic materials are far more abundant in the earth. It remains a great challenge in materials science today to develop a strong permanent magnet based on only 3d-orbital transition metals, because those metals lack both of the desirable features named above: the large spin-orbit interaction and the strong magnetic anisotropy caused by the 4f-orbital.

Tetragonally distorted FeCo is among the most promising candidates for a novel strong permanent magnet due to its relatively low, stable cost; a high magnetocrystalline anisotropy (\( K_u \)); the highest saturation magnetization among all transition metal alloys; and high Curie temperature. Recent first-principles calculations have predicted a high \( K_u \) for FeCo with a body-centered tetragonal (bct) structure.\textsuperscript{3-5} Various experimental studies have been carried out to grow ultrathin epitaxial bct FeCo on several buffer layers whose lattice constants were smaller than that of the body-centered cubic (bcc) FeCo structure.\textsuperscript{6-17} These studies have used thin films to investigate the basic properties of the bct FeCo that could be applied to a bulk permanent magnet in the future. The buffer layers were selected to introduce compressive stress into the FeCo lattice by way of the lattice mismatch between the buffer layer and the FeCo layer, resulting in the tetragonally distorted bct FeCo with axial ratio \( c/a > 1.00 \). The results of these studies revealed that the magnitude of \( K_u \) experimentally exceeded \( 10^6 \) J m\(^{-3}\) when the \( c/a \)-value of the FeCo
was in the range of $1.00 < c/a < \sqrt{2}$, where lattice constants ($a$, $c$) are based on the bct primitive cell, and the $c/a$-values of the bcc lattice and the face-centered cubic (fcc) lattice correspond to 1.00 and $\sqrt{2}$, respectively. Coercivity ($H_c$) is also an important parameter relative to the permanent magnet, and the magnitude of $H_c$ is observed to experimentally increase to several hundred kA m$^{-1}$ when it was nanofabricated into nanodots exhibiting diameters of less than 100 nm. Generally, the bct structure can be considered an intermediate structure between bcc and fcc. This relationship is known as the Bain transformation (bcc–bct–fcc), and typically occurs in martensitic materials.

In our previous report, FeCo films with elements V and N added were epitaxially grown on a Rh buffer layer, forming bct structure in films thicker than 5 nm. The $c/a$-value of the FeCo lattice depended on the N content, and the maximum $K_u$ of $1.24 \times 10^5$ J m$^{-3}$ was obtained at a composition of $(\text{Fe}_{0.5}\text{Co}_{0.5})_{90-0.5}\text{V}_{0.5}\text{N}_{0.5}$ with a $c/a$-value of 1.12. However, the Rh buffer layer also showed the capability to produce the bct FeCo lattice with $c/a > 1.00$, because the lattice constant of the Rh ($a_{Rh}/\sqrt{2}$) was shorter than that of the bcc FeCo ($a_{FeCo}$) when the structural relationship of Rh (001) $\langle 110 \rangle$ was realized. Subsequently the lattice mis-match could be $(a_{FeCo} - a_{Rb}/\sqrt{2})/a_{FeCo} \approx 0.05-0.07$, which is sufficient for the introduction of the bct FeCo lattice with $1.00 < c/a < \sqrt{2}$. Since in the previous report the effects of the Rh buffer layer remained to be fully investigated, the effects of the addition of V and N on the formation of the bct FeCo lattice remained unclear.

In this study, the FeCo was deposited directly on a MgO substrate without any other metallic layers, in order to avoid the effects of the buffer layers. Since the lattice constant of MgO was larger than that of the bcc FeCo, the MgO did not have the capability to produce a bct FeCo lattice with $c/a < 1.00$. Transmission electron microscopy (TEM) observation was carried out to clarify the effects of the addition of auxiliary elements on the formation of the bct FeCo structure.

II. EXPERIMENTS

FeCoVN films were deposited directly on the MgO substrate by DC magnetron co-sputtering at a base pressure of $10^{-7}$ Pa using Ar and N$_2$ as the sputtering gases. The total pressure of both gases was constant (0.1 Pa), and the N content in the produced films was controlled by altering the Ar and N$_2$ partial pressures between $(N_2/(Ar + N_2)) \times 100 = 0-50\%$. During the deposition process of the FeCoVN, the base composition of $(\text{Fe}_{0.5}\text{Co}_{0.5})_{90}V_{10}$ determined using an electron probe X-ray microanalyzer, was fixed, because the addition of ~10 atomic% (at.%) V produced the maximum value of $K_u$ in our previous report. The detailed substrate temperatures and the thickness $t$ of each film were as follows: The FeCoVN films, 20 nm thickness, were deposited on the single-crystalline MgO (100) substrate at 473 K, and the SiO$_2$ capping layer, of 5 nm thickness, was deposited on the FeCoVN surface at 298 K. The final composition of the produced FeCoVN films was determined by X-ray photoelectron spectroscopy, and was approximated as $(\text{Fe}_{25}\text{Co}_{25})_{90-0.2}V_{10-0.2}N_{x}$, where $0 < x < 9.6$ at.%. The V sputtering rate decreased faster than that of the Fe and Co as a function of $x$.

The crystal structure was investigated using conventional out-of-plane X-ray diffraction (XRD) in the $\theta$–2$\theta$ geometry, and conventional in-plane XRD with an in-plane scattering vector. In all XRD measurements, CuKa radiation was used. Cross-sectional scanning TEM (STEM) was used to investigate the atomic arrangement of the produced films, and the composition profile was analyzed using an energy dispersive X-ray detector (EDX) attached to the TEM equipment.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) respectively show the in-plane XRD patterns and the out-of-plane XRD patterns of the MgO (100) substrate/$(\text{Fe}_{0.5}\text{Co}_{0.5})_{90-0.2}V_{10-0.2}N_x$ ($0 < x < 9.6$ at.%, $t = 20$ nm)/SiO$_2$ ($t = 5$ nm) continuous films. The black dashed vertical line represents the peak position from the background (B.G.) of the MgO substrate. The lattice constant calculated for bcc FeCo structure was within the range of $0.284-0.286$ nm (bcc Fe$_{50}$Co$_{50}$, B2 Fe$_{50}$Co$_{50}$, and bcc Fe$_{46}$Co$_{53}$V$_{5-6}$), and that determined for fcc FeCo...
structure was within the range of 0.355–0.357 nm (fcc Fe\textsubscript{10}Co\textsubscript{90}, fcc Fe\textsubscript{46}Co\textsubscript{45}V\textsubscript{9}, and fcc Co\textsubscript{75}V\textsubscript{25}). The expected bcc FeCo (200), fcc FeCo (220), fcc FeCo (002), and bcc FeCo (002) diffraction angles were calculated from the reported values, and the expected peak positions are denoted by red dashed vertical lines. The red arrows represent the experimental peak positions. It is understood that the FeCoVN [100] axis is parallel to the [110] axes of the MgO substrate from Figure 1(a). Figure 1(b) indicates that the FeCoVN epitaxially grew on the MgO substrate, and that the FeCoVN [001] direction is perpendicular to the film plane. From these results, the structural relationship of MgO (001) [100]//FeCoVN (001) [110] is confirmed.

The in-plane and out-of-plane FeCoVN diffraction peaks denoted by the red arrows in Figure 1 range from 65° to 71° and 49° to 66°, respectively. This pattern indicates the existence of an intermediate structure between the bcc and fcc phases. No diffraction peaks corresponding to vanadium-nitrogen compounds (such as VN) were observed in either Figure 1(a) or 1(b); this absence suggests the formation of a solid FeCoVN solution without any precipitates. From these results, it can be concluded that the produced films underwent tetragonal distortion to form the bct structure stabilized by the interstitial N atoms.

Schematic illustrations of the bct and fcc structures are shown in Figures 2(a) and 2(b), respectively. We use the bct primitive cell for characterizing the lattice constants of the FeCo in order to understand the continuous structural change from bcc to fcc through bct structure with $1.00 < \frac{c}{a} < \sqrt{2}$. Figures 2(c) and 2(d) show the cross-sectional high-angle annular dark field (HAADF)-STEM images for the samples with $x = 1.7$ at.% and $x = 9.6$ at.%, respectively. Each atomic site of Fe, Co, V and N is not clear in these STEM images; however, no segregation was detected via the TEM–EDX analysis. We observed FeCo lattices of the (100) face for $x = 1.7$ at.%, and of the (110) face for $x = 9.6$ at.%. These faces correspond to the red faces drawn in Figures 2(a) and 2(b). Insets are enlarged images, in which the red bars and yellow bar correspond respectively to the lattice constants $a$ and $c$ of the sample with $x = 1.7$ at.%. The blue bars correspond to the lattice constant $c = \sqrt{2} a$ of the sample with $x = 9.6$ at.%. It is clear that the yellow bar (lattice constant $c$) is longer than the red bar (lattice constant $a$) in Figure 2(c), which we interpret as bct structure ($\frac{c}{a} = 1.12$) obtained for $x = 1.7$ at.%. In contrast, a square shape composed of blue bars is observed in Figure 2(d), which we interpret as fcc structure ($\frac{c}{a} = \sqrt{2}$) obtained for $x = 9.6$ at.%. 

**FIG. 2.** Schematic illustrations of (a) bct and (b) fcc structure with labels for the lattice constants ($a$, $c$) based on the bct primitive cell, represented by the red atoms. HAADF-STEM images in the FeCo layer with (c) (100) face of the sample for $x = 1.7$ at.%, and (d) (110) face of the sample for $x = 9.6$ at.%. These (100) and (110) faces correspond to the illustrations of red faces in (a) and (b), respectively. Insets are enlarged images. Red bars, yellow bar, and blue bars correspond to the lengths of the lattice constants ($a$, $c$) of the produced FeCo lattices.
Figures 3(a) and 3(b) show the N content (x)-dependences of the lattice constants a and c, as well as the axial ratio c/a of the MgO (100) substrate/(Fe₆₅Co₃₅)₀ₓ₋₀.₂V₁₀₋ₓNₓ (0 ≤ x ≤ 9.6 at.%, t = 20 nm)/SiO₂ (t = 5 nm) continuous films. The lattice constant a was estimated from the FeCo (200) peak positions observed in the in-plane XRD patterns shown in Figure 1(a), while lattice constant c was estimated from the FeCo (602) peak positions observed in the out-of-plane XRD patterns shown in Figure 1(b). The obtained lattice constants a and c were consistent with the values estimated from the STEM images shown in Figures 2(a) and 2(b). Previous results relating to FeCoVN deposited on a Rh buffer layer (MgO sub./Rh/FeCoVN (t = 20 nm)/SiO₂) are also plotted using open symbols. The obtained a and c values were consistent with each other for both samples, with or without the Rh buffer layer. With increasing x, the a-value decreased, while the c-value increased, and finally both values approached that of the fcc structure. The obtained c/a-value depended on x, and increased from 1.02 (bcc) for x = 0 at.% to 1.43 (fcc) for x = 9.6 at.%, so the bcc–bct–fcc transformation can be understood as tunable by N addition. The x-dependence trends of the c/a-values were consistent with each other for both samples, with or without the Rh buffer layer. It can therefore be concluded that the bcc–bct–fcc structural transformation was affected by N addition, and not affected by the lattice mismatch between the buffer layer and the FeCo layer in the thicker region (t > 5 nm).

IV. CONCLUSIONS

The bcc–bct–fcc transformation of FeCoVN films (t = 20 nm) were investigated using XRD and TEM. The FeCoVN crystal structure's transformation from bcc to fcc through bct structure was dependent on N content (x). TEM observation revealed that bct structure with c/a = 1.12 was obtained for x = 1.7 at.%, while fcc structure with c/a = √2 was obtained for x = 9.6 at.%. The c/a-values depended on x, so the bcc–bct–fcc transformation can be understood as tunable by N content. Since the x-dependence trends in c/a-values were consistent for both samples, with or without buffer layers, it can be concluded that the transformation of the bcc–bct–fcc structures were affected by N addition, rather than by the buffer layers.

ACKNOWLEDGMENTS

This work was supported by the New Energy and Industrial Technology Development Organization (NEDO), Japan. The authors would like to thank Enago for the English language review.

REFERENCES

1. N. Jones, Nature 472, 22 (2011).
2. J. D. Coey, Scripta Materialia 67, 524 (2012).
3. T. Burkert, L. Nordström, O. Eriksson, and O. Heinonen, Physical Review Letters 93, 027203 (2004).
4. Y. Kota and A. Sakuma, Journal of Applied Physics Express 5, 113002 (2012).
5. K. Hyodo, Y. Kota, and A. Sakuma, Journal of the Magnetics Society Japan 39, 37 (2013).
6. G. Andersson, T. Burkert, P. Warnick, M. Bjoerck, B. Sanyal, C. Chacon, C. Zlotea, L. Nordstrom, P. Nordblad, and O. Eriksson, Physical Review Letters 96, 037205 (2006).
7. F. Yildiz, M. Przybylski, X.-D. Ma, and J. Kirschner, Physical Review B 80, 064415 (2009).
8. L. Reichel, L. Schultz, D. Pohl, S. Oswald, S. Fähler, M. Werwinski, A. Edström, E. K. Delcze-Czirak, and J. Ruz, J. of Physics: Condensed Matter 27, 476002 (2015).
9. T. Ohnozaki, T. Kojima, M. Kotsugi, T. Ohkochi, M. Mizuguchi, and K. Takahashi, J. Appl. Phys. 115, 043908 (2014).
10. B. Luo, J. W. Jung, and M. Sahashi, IEEE Transactions on Magnetics 50, 1 (2014).
11. B. Wang, H. Oomiya, A. Arakawa, T. Hasegawa, H. Sasaki, and S. Ishio, Journal of Applied Physics 117, 17C709 (2015).
12. M. Matsuura, N. Tezuka, and S. Sugimoto, Journal of Applied Physics 117, 17A738 (2015).
13. H. Oomiya, B. Wang, S. Yoshida, T. Kagoshima, K. Takahashi, S. Kanatani, L. Zhang, L. Liu, T. Hasegawa, K. Hayasaka, S. Saito, N. Inami, T. Ueno, K. Ono, and S. Ishio, Journal of Physics D: Applied Physics 48, 475003 (2015).
14. T. Hasegawa, S. Kanatani, M. Kazaana, K. Takahashi, K. Kumagai, M. Hirao, and S. Ishio, Scientific Reports 7, 13215 (2017).
15. K. Takahashi, M. Sakamoto, K. Kumagai, T. Hasegawa, and S. Ishio, Journal of Physics D: Applied Physics 51, 065005 (2018).
16 R. Mandal, J. W. Jung, K. Masuda, Y. K. Takahashi, Y. Sakuraba, S. Kasai, Y. Miura, T. Ohkubo, and K. Hono, Applied Physics Letters 113, 232406 (2018).
17 T. Hasegawa, T. Niibori, Y. Takemasa, and M. Oikawa, Scientific Reports 9, 5248 (2019).
18 J. S. Bowles and C. M. Wayman, Metallurgical and Materials Transactions 3, 1113–1121 (1972).
19 B. R. Cuenya, M. Doi, S. Lobus, R. Courths, and K. Keune, Surface Science 493, 338–360 (2001).
20 G. Pourroy, S. Lakamp, and S. Vilminot, Journal of Alloys and Compounds 244, 90–93 (1996).
21 Y. Aoki and M. Yamamoto, Physica Status Solidi 33, 625–632 (1976).
22 D. L. Martin and A. H. Geisler, Transactions of American Society for Metals 44, 461–483 (1952).
23 T. Onozuka, S. Yamaguchi, M. Hirabayashi, and T. Wakiyama, Journal of the Physical Society of Japan 37, 687–693 (1974).
24 W. C. Ellis, and E. S. Greiner, Transactions of American Society for Metals 29, 415–432 (1941).