Microstructure of hcp–Ni(1100)/bcc–Cr(211) Bi-layer Film Grown on MgO(110) Substrate

Mitsuru Ohtake, Yoichi Sato, Jumpei Higuchi and Masaaki Futamoto
Faculty of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan
E-mail: ohtake@futamoto.elect.chuo-u.ac.jp

Abstract. A Ni epitaxial film with hcp(1100) single-crystal structure is obtained on a Cr(211) underlayer hetero-epitaxially grown on an MgO(110) single-crystal substrate in an early stage of film growth by ultra high vacuum rf magnetron sputtering. Reflection high energy electron diffraction (RHEED) observation indicates that the metastable hcp–Ni crystal tends to transform into more stable fcc crystal with increasing the film thickness. The crystallographic orientation relationship between the hcp and the fcc crystals is determined by RHEED and φ-scan X-ray diffraction. High-resolution transmission electron microscopy shows that the hcp and the fcc crystals exist separately on the Cr underlayer. The lattice constants of hcp–Ni crystal are determined from X-ray diffraction analysis as \( a = 0.249 \text{ nm}, \ c = 0.415 \text{ nm}, \) and \( c/a = 1.67. \)

1. Introduction

3d ferromagnetic transition metal thin films have been widely studied for applications such as magnetic recording media, magnetic heads, etc. Metastable 3d transition metal films have also recently attracted much attention for practical applications like tunneling magnetoresistance devices [1]. The magnetic properties are greatly affected by their crystal structures. Ni is a typical soft magnetic material with fcc structure. hcp–Ni crystal is metastable and does not appear in the bulk phase diagram. A theoretical calculation predicts that the magnetic anisotropy of bulk hcp–Ni crystal is very similar to that of bulk hcp–Co crystal [2]. Preparation of hcp–Ni crystal has been reported in the forms of nanoparticles and thin films [3]–[7]. However, parts of the hcp crystal tend to transform into more stable fcc structure during sample preparation processes, and these samples generally include large volume of fcc phase.

Recently, epitaxial thin film growth has made it possible to prepare metastable structures. In our previous studies, hcp–Ni [8]–[10] and hcp–permalloy [11] epitaxial films have been prepared on Au(100) underlayers at temperatures below 300 and 400 °C, respectively. The films consisted of two types of hcp(1120) variants whose orientations were rotated around the film normal by 90° each other. However, the hcp crystal also transformed into fcc structure. X-ray pole figure analysis showed that the crystallographic orientation relationships between the hcp and the fcc crystals were hcp(1120)[1100] || fcc(011)[211] and fcc(011)[2T1] [12]. In order to investigate the hcp–Ni film growth and the transformation from hcp to fcc phase in detail, it is desirable to employ an hcp–Ni single-crystal film. bcc–Cr(211) has been frequently used as an underlayer to prepare an hcp–Co(1100) single-crystal film with the c-axis parallel to the substrate surface [13]. The bcc–Cr(211) is expected also to promote the growth of hcp–Ni single-crystal film. In the present study, a Cr(211) underlayer hetero-epitaxially grown on an MgO(110) single-crystal substrate is employed to prepare an hcp–Ni single-crystal film. The film growth and the detailed film microstructure are investigated.
underlayer was determined by RHEED observation as follows, of bcc–Cr(211) on MgO(110). The epitaxial orientation relationships between the substrate and the deposited on the substrate at 300 °C. The substrate temperature was used to promote epitaxial growth for both materials.

The film layer structure was Ni(40 nm)/Cr(10 nm)/MgO(110). A 10-nm-thick Cr underlayer was deposited on the substrate at 300 °C. The substrate temperature was used to promote epitaxial growth of bcc–Cr(211) on MgO(110). The epitaxial orientation relationships between the substrate and the underlayer was determined by RHEED observation as follows, Cr(211) || MgO(110) || MgO(110) (Type I), Cr(211) || MgO(110) || MgO(110) (Type J).

The Cr(211) underlayer consists of two types of variants whose orientations are rotated around the film normal by 180° each other, as shown in figures 1(e)–(g). A 40-nm-thick Ni film was deposited on the Cr underlayer at room temperature.

The surface structure during Ni rf–sputter deposition process was studied by RHEED. The structural properties were investigated by out-of-plane (2θ/ω–scan), in-plane (2θ/φ–scan), and φ–scan X-ray diffraction (XRD) with Cu–Kα radiation (λ=0.15418 nm). The surface morphology and the cross-sectional microstructure were respectively observed by AFM and transmission electron microscopy (TEM). The TEM sample was first thinned mechanically and then ion-milled to be transparent for the electron beam accelerated at 300 kV.

3. Results and discussion

A Ni epitaxial thin film was obtained on a bcc–Cr(211) underlayer. Figures 2(a) and (b) show the RHEED patterns observed in the Ni rf–sputter deposition process. A clear diffraction pattern of hcp(1100) reflection shown in the RHEED spot map of figure 2(e) is observed in an early stage of Ni film growth, as shown in figure 2(a). An hcp–Ni(1100) single-crystal film is obtained on the underlayer. The epitaxial orientation relationship between the underlayer and the hcp–Ni crystal is determined by RHEED observation as follows,
Figure 2. (a,b) RHEED patterns observed for a Ni film grown on a Cr(211) underlayer. The film thicknesses are (a) 2 nm (b) 40 nm. (c,d) RHEED intensity profiles along the dotted lines in (a,b), respectively. (e) RHEED spot map of hcp(1100). (f) Film thickness dependence on the RHEED spot peak intensity ratio of Spot–P to Spot–Q shown in (a,b). (g) RHEED spot map of fcc(211). The incident electron beam is parallel to the MgO[001] direction. (h,i) Epitaxial orientation relationship and the lattice mismatches of Ni(1100) || Cr(211). The lattice mismatches are calculated from the lattice constants of the Cr crystal and the hcp–Ni film prepared in the present study. (k,l) Crystallographic orientation relationship between the hcp–Ni(1100) crystal and the fcc–Ni(211) crystal transformed from the hcp–Ni crystal. The schematic models are viewed along (h) the MgO[110] and (i) the MgO[001] directions. The dotted lines in (i,l) show variant boundaries. The symbols, I, J, M, and N, respectively correspond to the orientation relationships of Type I, J, M, and N explained in the text. The symbols, A, B, and C, show the stacking sequence of closed packed plane.

Ni(1100)[0001] || Cr(211)[01\bar{1}] Type I and Cr(211)[0\bar{1}1] Type J || MgO(110)[001].

With increasing the film thickness, the RHEED spot intensities of 3300, 2110, 1120, and 2240 become stronger, whereas those of 2200, 3110, 3120, 2130, and 1230 weaken. The RHEED data suggest that another pattern overlaps with the hcp(1100) pattern. The pattern of increasing spot intensity is analyzed to be due to an overlap of two fcc(211) reflections, as shown by the spots, M and N, in the spot map of figure 2(g). The hcp structure in the Ni film is apparently transforming into more stable fcc structure. The transformed fcc–Ni crystal is formed on the Cr(211) underlayer in the following orientation relationships [figures 2(k) and (l)],

Ni(211)[\bar{1}1\bar{1}] || Ni(1100)[0001] || MgO(110)[001] (Type M),
Ni(211)[11\bar{1}] || Ni(1100)[0001] || MgO(110)[001] (Type N).

Figure 2(f) shows the film thickness dependence on the RHEED spot peak intensity ratio of 3300 (Spot–P) to 2200 (Spot–Q) estimated from the RHEED intensity profiles, observed, for example, as figures 2(c) and (d). The ratio gradually increases with increasing the film thickness. The increase in the intensity ratio shows that the ratio of fcc to hcp crystal exposed to the film surface increases with increasing the film thickness.

In order to confirm the orientation relationship between the hcp and the transformed fcc crystals, \(\phi\)-scan XRD analysis was performed. Figure 3 shows the \(\phi\)-scan XRD spectra of MgO[200], Cr[200], hcp–Ni{1010}, and fcc–Ni{111} poles. For the spectra of MgO[200] and hcp–Ni{1010}
poles, two-fold symmetrical diffraction peaks are recognized. For the spectra of Cr\{200\} and fcc–Ni\{111\} poles, two diffraction peaks which originate from the Type I and the Type J bcc–Cr(211) variants and the Type M and the Type N fcc–Ni(211) variants are observed with 180° separation, respectively. The orientation relationship between the hcp–Ni and the fcc–Ni crystals expected from the RHEED study is confirmed by XRD analysis.

Figures 4(a)–(d) show the out-of-plane and the in-plane XRD spectra of the Ni/Cr/MgO specimen. hcp–Ni\{1\ 0\ 0\} out-of-plane, hcp–Ni\{0002\} and/or fcc–Ni\{1\ 1\ 1\} in-plane, hcp–Ni\{1\ 1\ 0\ 0\} and/or fcc–Ni\{022\} in-plane, and hcp–Ni\{1\ 1\ 2\ 2\} in-plane XRD reflections are clearly recognized. The lattice constant, \(a\), of the hcp–Ni crystal is determined from the Ni(1\ 1\ 0\ 0) XRD peak to be \(2d_{\text{Ni}(1\ 1\ 0\ 0)}/3 = 0.249\) nm. The lattice constant, \(c\), is calculated from the lattice constant, \(a\), and the lattice spacing, \(d_{\text{Ni(1\ 1\ 2\ 2)}}\), to be 0.415 nm, by considering the structure shown in figure 4(c). The \(c/a\) ratio is thus 1.67.

Figure 5(a) shows the AFM image of the Ni/Cr/MgO specimen. Small islands with rounded tops of 10–30 nm in diameter are observed. Figure 5(b) shows the cross-sectional TEM image observed along the MgO[1\ 1\ 0\] direction. Sharp boundaries are recognizable between the MgO substrate and the Cr underlayer and between the underlayer and the Ni film. Figure 6(a) shows the high-resolution cross-sectional TEM image around the Ni/Cr interface. hcp–Ni and fcc–Ni crystals exist separately on the Cr underlayer and between the underlayer and the Ni film. Figures 4(a)–(d) show the out-of-plane and (b,c,d) in-plane XRD spectra of a Ni/Cr/MgO(1\ 1\ 0) specimen. The in-plane XRD is measured by making the scattering vector parallel to (b) the MgO[0\ 0\ 2], (c) the MgO[2\ 2\ 0], and (d) the Ni[1\ 1\ 2\ 2] directions, and the incident X-ray angle is fixed at 0.4°. The intensity is shown in a logarithmic scale. (e) Schematic model of relationship between Ni(1\ 1\ 0\ 0) and Ni(1\ 1\ 2\ 2).

Figure 3. \(\phi\)-scan XRD spectra of (a) MgO[2\ 0\ 0], (b) Cr[2\ 0\ 0], (c) hcp–Ni[1\ 0\ 1\ 0], and (d) fcc–Ni{1\ 1\ 1} poles obtained from a Ni/Cr/MgO specimen. The intensity is shown in a logarithmic scale. The symbols, I, J, M and N, respectively correspond to the orientation relationships of Type I, J, M, and N explained in the text.

Figure 4. (a) Out-of-plane and (b,c,d) in-plane XRD spectra of a Ni/Cr/MgO specimen. The in-plane XRD is measured by making the scattering vector parallel to (b) the MgO[002], (c) the MgO[220], and (d) the Ni[1122] directions, and the incident X-ray angle is fixed at 0.4°. The intensity is shown in a logarithmic scale. (e) Schematic model of relationship between Ni(1\ 1\ 0\ 0) and Ni(1\ 1\ 2\ 2).

Figure 5. (a) AFM and (b) cross-sectional TEM images of a Ni/Cr/MgO specimen observed along the MgO[1\ 1\ 0] and the MgO[1\ 1\ 0] directions, respectively.
Figure 6. (a) Cross-sectional high-resolution TEM image around the Ni/Cr interface. The image is observed along the MgO\([\overline{1}00]\) direction. The dotted lines in (a) show variant boundaries. (b,c,d) Enlarged views and (b',c',d') 2D FFT maps of the areas surrounded by white square lines in (a).

4. Conclusion

A Ni epitaxial film with hcp\([\overline{1}00]\) orientation is obtained on a Cr(211) underlayer formed on an MgO(110) substrate in a early stage of film growth. With increasing the film thickness, Ni crystals with (211) orientations with fcc structure start to coexist with the hcp structure and the fcc/hcp ratio increases. This is due to a phase transformation from metastable hcp to more stable fcc structure. The resulting film consists of a mixture of hcp and fcc crystals. The crystallographic orientation relationships between the hcp and the transformed fcc crystals are Ni(211)[1\_11] \parallel Ni(11\_00)[0001]. The lattice constants of hcp–Ni crystal are determined as \(a=0.249\) nm, \(c=0.415\) nm, and \(c/a=1.67\).

Acknowledgements

A part of this work was supported by NEDO-Japan and STFJ (Science and Technology Foundation of Japan). M. Ohtake is a Research Fellow of the Japan Society for the Promotion of Science.

References

[1] Yuasa S, Fukushima A, Kubota H, Suzuki Y and Ando K 2006 Appl. Phys. Lett. 89 042505
[2] Papaconstantopoulos D A, Fry J L and Brener N E 1989 Phys. Rev. B 39 2526
[3] Hemenger P and Weik H 1965 Acta Crystallogr. 19 690
[4] Carturan G, Cocco G, Enzo S, Ganzerla R and Lenarda M 1988 Mater. Lett. 7 47
[5] González V R et al. 2007 J. Solid State. Chem. 180 22
[6] Tian W et al. 2005 Appl. Phys. Lett. 86 131915
[7] Tanaka T, Ohtake M, Kirino F and Futamoto M 2009 IEEE Trans. Magn. 45 2515
[8] Ohtake M, Tanaka T, Kirino F and Futamoto M 2010 J. Phys. Conf. Ser. 200 072072
[9] Ohtake M, Tanaka T, Kirino F and Futamoto M 2010 J. Appl. Phys. 107 09E310
[10] Ohtake M, Tanaka T, Kirino F and Futamoto M 2010 J. Magn. Soc. Jpn. 34 267
[11] Tanaka T, Ohtake M, Kirino F and Futamoto M 2010 IEEE Trans. Magn. 46 1947
[12] Sato Y, Ohtake M, Higuchi J, Tanaka T, Kirino F, Futamoto M 2010 Structural Analysis of hcp–Ni and hcp–NiFe Thin Films Epitaxially Grown on Au(100) Single-Crystals Abstr. ISAMMA 2010 (Sendai, Japan, 12–16 July 2010) PF–03
[13] Nakamura A and Futamoto M 1993 Jpn. J. Appl. Phys. 32 L1410