Structure Characterization of Fe, Co, and Ni Thin Films
Epitaxially Grown on GaAs(111) Substrate

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Fe, Co, and Ni films of 40 nm thickness are prepared on GaAs(111) single-crystal substrates at room temperature by using a radio-frequency magnetron sputtering system. The film growth behavior and the crystallographic properties are investigated by in-situ reflection high-energy electron diffraction and pole-figure X-ray diffraction. Bcc single-crystals of (111) orientation are formed on the substrates for all the film materials, though the bcc structure is metastable for Co and Ni materials. The metastable structure is stabilized through heteroepitaxial growth. Fe films possess bcc structure for the investigated thickness range. On the contrary, the bcc-Co and the bcc-Ni crystals, respectively, start to transform into hcp and fcc structures, as the thickness is increased beyond 2 nm. The phase transformations occur through atomic displacements from the close-packed planes of bcc(110), bcc(101), and bcc(011), which are perpendicular to the substrate surface, to hcp(0001) and fcc(111) close-packed planes. The crystallographic orientation relationships of hcp and fcc crystals with respect to bcc crystal are similar to the Kurdjumov-Sachs relationship.

Key words: 3d transition metals, epitaxial growth, thin films, GaAs(111) substrate, metastable bcc structure, phase transformation

1. Introduction

Hybrid structure of ferromagnetic metal and semiconductor materials has been investigated for spin electronics applications like spin-dependent field effect transistors, etc. Bcc phase is stable for Fe, whereas that is metastable for Co and Ni at room temperature (RT). It has been reported that magnetic tunnel junction elements prepared by using Co films with metastable bcc structure show high tunnel magnetoresistance ratios¹-². The magnetic and electronic properties vary depending on the crystal structure. It is thus important to understand the formation conditions of magnetic films with metastable bcc structure.

Metastable bcc phase formation has been recognized for very thin Co³-⁵ and Ni⁶ films on GaAs single-crystal substrates of (100) and (110) orientations around RT deposited by molecular beam epitaxy (MBE). With increasing the thickness, most of the bcc-Co and the bcc-Ni crystals transformed into more stable hcp or fcc structure and the resulting films involved large volumes of hcp or fcc crystals. Recently, we succeeded in the formation of Co and Ni films with bcc structure on GaAs(100)⁷-⁹ and GaAs(110)⁹b substrates by sputtering, which is more suitable than MBE for mass-production applications. The thickness stability of bcc phase and the transformation process to hcp or fcc structure were investigated. With increasing the thickness beyond 2 nm, the bcc crystals formed on GaAs(100) and GaAs(110) substrates, respectively, started to transform into stable structures through atomic displacements parallel to the six bcc(110) close-packed planes and the four bcc(101), bcc(011), bcc(011), and bcc(101) planes which are 60° inclined from the substrate surface. The slide planes, where the phase transformation occurs, differ depending on the substrate orientation.

In our previous study¹⁰, Co films were prepared on GaAs(111) substrates by varying the substrate temperature from RT to 600 °C. The film structure was investigated by reflection high-energy electron diffraction (RHEED), where the incident electron beam was parallel to only GaAs[110]. In the early stage of film growth at temperatures lower than 200 °C, Co(111) crystals with bcc structure were formed. With increasing the thickness, the bcc(111) crystals started to transform into the stable phase, similar to the cases of Co films formed on GaAs(100)⁷-⁹ and GaAs(110)⁹b substrates. When the substrate temperature was higher than 400 °C, Ga atoms of substrate seemed to diffuse into the Co films and an ordered alloy with bcc-based B2 structure was formed.

In the present study, Fe, Co, and Ni films are prepared on GaAs(111) substrates at RT under similar deposition conditions. The detailed growth behaviors are studied by RHEED using two kinds of incident electron beam, GaAs[110] and GaAs[112]. The resulting structure is characterized by out-of-plane, in-plane, and pole-figure X-ray diffractions (XRDs). The influences of film material and thickness on the crystallographic properties are systematically investigated.

2. Experimental Procedure

A radio frequency (RF) magnetron sputtering system equipped with an RHEED facility was employed. The base pressure was lower than 4 × 10⁻⁷ Pa. GaAs(111) substrates were heated at 600 °C before deposition to obtain clean surfaces. Figures 1(a) and 2(a) show the RHEED patterns observed for a GaAs substrate after annealing. The incident electron beam is parallel to GaAs[110] in Fig. 1(a), whereas that is parallel to GaAs[112] in Fig. 2(a). Diffraction patterns consisting of spots are observed, which may suggest that the substrate surface involves an atomic level roughness. Figures 1(b) and 2(b) show the schematic diagrams of diffraction patterns of a B2(111) single-crystal surface calculated by using the two kinds of electron beam direction. The experimental data of Figs. 1(a) and 2(a)
materials. The films grow epitaxially on the substrates. RHEED patterns are recognized for all the film thickness prepared on GaAs(111) substrates. Clear RHEED patterns observed for Fe, Co, and Ni films of 1 and (c-4)–(e-4) 40 nm. (f) Schematic diagram of a bcc(111) single-crystal with reconstructed surface of \( p(3\times3) \). The incident electron beam is parallel to [110].

agree with the simulation results of Figs. 1(b) and 2(b), respectively. A clean GaAs(111) surface with \( B3 \) structure is thus obtained. A chemical analysis is necessary to determine the kind of atom terminated at the surface.

Fe, Co, and Ni films were prepared on the substrates at RT by varying the thickness in a range from 1 to 40 nm. The distance between target and substrate was fixed at 150 mm. The Ar gas pressure was kept constant at 0.67 Pa. Fe, Co, and Ni targets of 3 inch diameter were employed and the respective RF powers were fixed at 48, 54, and 50 W, where the deposition rate was 0.02 nm/s for all the materials.

The surface structure was studied by RHEED. The resulting film structure was investigated by XRDs with Cu-K\( \alpha \) radiation (\( \lambda = 0.15418 \) nm). The magnetization curves were measured by vibrating sample magnetometry.

3. Results and Discussion

Figures 1(c-1)–(e-1) and 2(c-1)–(e-1) show the RHEED patterns observed for Fe, Co, and Ni films of 1 nm thickness prepared on GaAs(111) substrates. Clear RHEED patterns are recognized for all the film materials. The films grow epitaxially on the substrates. Figures 1(f) and 2(f) show the schematic diagrams of RHEED patterns simulated for a bcc(111) single-crystal, where the open circle spots correspond to the reflections from reconstructed surface of \( p(3\times3) \). The RHEED patterns observed for Fe film are in agreement with the simulated patterns without open circle spots, whereas those observed for Co and Ni films are matching with the simulated patterns involving open circle spots. bcc structure is thus stabilized not only for the Fe film but also for the Co and Ni films through heteroepitaxial growth on GaAs(111) substrate, similar to the cases of films prepared on GaAs(100)\(^{7,8} \) and GaAs(110)\(^{9} \) substrates. The epitaxial relationship is determined by RHEED as bcc(111)[1\( \overline{1} \)0] \( \parallel \) GaAs(111)[1\( \overline{1} \)0].

Figures 1(c-2)–(e-4) and 2(c-2)–(e-4) show the RHEED patterns observed for Fe films thicker than 2 nm. RHEED patterns corresponding to the diffraction patterns simulated for bcc(111) surface remain unchanged till the end of 40-nm-thick film formation. Figures 1(d-2)–(e-4) and 2(d-2)–(e-4) show the RHEED patterns observed for Co and Ni films thicker than 2 nm. As the thickness increases, the RHEED spots become broader and diffraction spots different from those of bcc(111) surface appear. The result indicates that a phase transformation is taking place.

When a bulk bcc material transforms into fcc
structure, there are two possibilities in the crystallographic orientation relationship, Nishiyama-Wasserman (NW)\textsuperscript{11,12} and Kurdjumov-Sachs (KS)\textsuperscript{13}. The phase transformation occurs through atomic displacements from six bcc(110) close-packed planes to fcc(111) close-packed planes. The crystallographic orientation relationship of bcc-hcp phase transformation seems similar to that of bcc-fcc transformation, as shown in Fig. 3. The phase transformation in Co film is considered to occur through atomic displacements from all the six (110) close-packed planes, from the three close-packed planes of bcc(110), bcc(101), and bcc(011) which are 35° canted from the substrate surface, or from the three close-packed planes of bcc(110), bcc(101), and bcc(011) which are perpendicular to the substrate surface. Figures 4(a) and 5(a) show the schematic diagrams of RHEED patterns calculated for hcp crystals transformed through atomic displacements from the bcc(110), bcc(101), and bcc(011) planes. Figures 4(b) and 5(b) show the schematic diagrams of RHEED patterns simulated for hcp crystals transformed through atomic displacements from the bcc(110), bcc(101), and bcc(011) planes. The RHEED patterns observed for Co films thicker than 2 nm [Figs. 1(d-2)–(d-4), 2(d-2)–(d-4)] agree with the simulated patterns of Figs. 4(b-3) and 5(b-3), as shown in Fig. 6. The result shows that the phase transformation is not taking place through atomic displacements from the six bcc(110) planes but from the three close-packed planes of bcc(110), bcc(101), and bcc(011) in the KS-2
relationship. Therefore, the Co films thicker than 2 nm involve three hcp variants whose c axes are lying in the film plane and rotated around the film normal by 120° each other. The transformation direction seems to be influenced by the strain caused by accommodation of the lattice mismatch between the film and the substrate. The crystallographic orientation relationships are determined as follows,

\[
\begin{align*}
\text{hcp}(0001)[01\overline{1}] & \parallel \text{bcc}(1\overline{1}0)[1\overline{1}]1, \\
\text{hcp}(0001)[01\overline{1}] & \parallel \text{bcc}(10\overline{1})[1\overline{1}], \\
\text{hcp}(0001)[01\overline{1}] & \parallel \text{bcc}(01\overline{1})[1\overline{1}].
\end{align*}
\]

The crystallographic relationships are slightly different from the results reported for Co film growth on GaAs(111) substrate\(^{10}\). In the present study, two different incident electron beam directions are employed to accurately determine the relationships, since broad RHEED spots may include position errors.

Phase transformation in Ni film is also considered to occur through atomic displacements from the three close-packed planes of bcc(110), bcc(101), and bcc(011) to fcc(111) close-packed plane. However, there are two kinds of atomic stacking sequence of fcc(111) plane along the fcc[111] direction, ABCABC... and ACBACB..., for an fcc crystal, while that of hcp(0001) plane along the hcp[0001] direction is only ABAB... Figure 7 summarizes the crystallographic orientation relationships of bcc-fcc phase transformation. Figures 8(a) and 9(a) show the schematic diagrams of RHEED patterns simulated for fcc crystals with the atomic stacking sequence of ABCABC... transformed through atomic displacements from the bcc(110), bcc(101), and bcc(011) planes. Figures 8(b) and 9(b) show the schematic diagrams of RHEED patterns calculated for fcc crystals with the ACBACB... stacking sequence transformed through atomic displacements from the bcc(110), bcc(101), and bcc(011) planes. Figures 10(a) and (b) show the RHEED patterns observed for the 10-nm-thick Ni film [Figs. 10(a)] overlapped with the simulated patterns of fcc crystals with stacking

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**Figure 7** Crystallographic orientation relationships of bcc-fcc phase transformation.

**Figure 8** Schematic diagrams of RHEED patterns simulated for fcc crystals with the atomic stacking sequences of (a) ABCABC... and (b) ACBACB... along fcc[111] transformed from a bcc(111) crystal epitaxially grown on GaAs(111) substrate through atomic displacements from bcc(110), bcc(101), and bcc(011) planes in [(a)-1], [(b)-1] the NW, [(a)-2], [(b)-2] the KS-1, and [(a)-3], [(b)-3] KS-2 relationships. The incident electron beam is parallel to GaAs(110).

**Figure 9** Schematic diagrams of RHEED patterns simulated for fcc crystals with the atomic stacking sequences of (a) ABCABC... and (b) ACBACB... along fcc[111] transformed from a bcc(111) crystal epitaxially grown on GaAs(111) substrate through atomic displacements from bcc(110), bcc(101), and bcc(011) planes in [(a)-1], [(b)-1] the NW, [(a)-2], [(b)-2] the KS-1, and [(a)-3], [(b)-3] KS-2 relationships. The incident electron beam is parallel to GaAs(112).

**Figure 10** RHEED patterns observed for a 10 nm-thick Ni film prepared on GaAs(111) substrate [Figs. 10(a)-3], [2(e)-3] overlapped with reflection spots simulated for fcc crystals with the stacking sequences of ABCABC... and ACBACB... along fcc[111] transformed through atomic displacements from bcc(110), bcc(101) and, bcc(011) planes in the KS-2 relationship [Figs. 8(a)-3], [8(b)-3], [9(a)-3], [9(b)-3]. The incident electron beam is parallel to (a) GaAs[110] or (b) GaAs[112].
sequences of ABCABC... and ACBACB... which are transformed from the bcc(110), bcc(101), and bcc(011) planes in the KS-2 relationship [Figs. 8(a-3), 8(b-3), 9(a-3), 9(b-3)]. The observed RHEED patterns are well matched with the calculated patterns. The crystallographic orientation relationships are thus determined as follows,

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\begin{align*}
\text{fcc}(111)[011] & \parallel \text{bcc}(110)[111], \\
\text{fcc}(111)[011] & \parallel \text{bcc}(101)[111], \\
\text{fcc}(111)[011] & \parallel \text{bcc}(011)[111], \\
\text{fcc}(111)[011] & \parallel \text{bcc}(110)[111], \\
\text{fcc}(111)[011] & \parallel \text{bcc}(101)[111], \\
\end{align*}
\]

The slide planes and the thickness, where the transformation from bcc to hcp or fcc phase starts, are similar between Co and Ni films. Furthermore, the critical thickness of around 2 nm is almost similar to those observed for Co and Ni films prepared on GaAs(100)⁷,⁸ and GaAs(110)⁹ substrates, though the crystallographic orientation relationships of hcp or fcc crystals with respect to bcc crystal are different in the cases of film deposition on GaAs(100), GaAs(110), and GaAs(111) substrates.

Figures 11(a) and 12(a) show the out-of-plane and the in-plane XRD patterns of 40-nm-thick Fe film formed on GaAs(111) substrate. Here, the scattering vector of in-plane XRD is parallel to GaAs[110]. Fe(222)bcc reflection is clearly observed in addition to GaAs(444) reflection in the out-of-plane pattern, whereas Fe(110)bcc reflection is recognized in the in-plane pattern. The out-of-plane and the in-plane XRDs confirm the epitaxial orientation relationship determined by RHEED. Figures 11(b) and (c) show the out-of-plane XRD patterns of 40-nm-thick Co and Ni films, respectively. Reflections from the hcp and the fcc crystals transformed from the bcc structure are not recognized for the Co and the Ni films, since the low index planes of transformed hcp-Co and fcc-Ni crystals are not parallel to the substrate surface. Figures 12(b) and (c) show the in-plane XRD patterns of 40-nm-thick Co and Ni films, respectively. Reflections from the hcp and the fcc crystals transformed from the bcc structure are not recognized for the Co and the Ni films, whereas fcc(0002) reflection is observed for the Co film, whereas fcc(111) reflection is recognized for the Ni film. The out-of-plane and the in-plane XRDs confirm that the transformations occur from the bcc(110), bcc(101), and bcc(011) slide planes which are perpendicular to the substrate surface.

Figures 13(a)–(c) show the pole-figure XRD patterns of 40-nm-thick Fe, Co, and Ni films measured by fixing the diffraction angle of 2θB at 47.5°, where GaAs(220) and hcp(011) reflections are expected to be detectable. The signals with the intensities smaller than 10 cps are subtracted. Figures 13(d) and (e), respectively, show the schematic diagrams of pole-figure XRD patterns simulated for a GaAs(111) substrate and the hcp crystals transformed from bcc structure in the orientation relationships determined by RHEED. The pole-figure XRD patterns of Fe and Ni films show three-fold symmetry, where GaAs(220) reflections are recognized at the tilt angle, α, of 55° and the rotation angles, β, of 120°, 240°, and 0°. The pole-figure XRD pattern of Co film shows six hcp[1101] reflections from the fcc crystals at the tilt angle, α, of 44°. The hcp reflections are not observed for the Ni film. Figures 14(a)–(c) show the pole-figure XRD patterns of 40-nm-thick Fe, Co, and Ni films measured by fixing the diffraction angle of 2θB at 51.8°, where GaAs(311) and fcc[001] reflections are expected to be detectable. The signals with the intensities smaller than 10 and 1 cps are subtracted for the respective films. Figures 14(d) and (e), respectively, show the schematic diagrams of pole-figure XRD patterns simulated for a GaAs(111) substrate and the fcc crystals transformed from bcc structure in the orientation relationships determined by RHEED. Reflections which originate from the GaAs substrate, are recognized around α = 10°, 32°, and 61° for all the films [Figs. 14(a–2), (b–2), and (c–1)]. Reflections, which originate from the fcc crystals, are observed around α ≈ 9°, 38° and 51° for the Ni film [Fig. 14(c–1)]. On the other hand, the fcc reflections are not...
observed for the Co film. Therefore, the bcc crystals in Co and Ni films are apparently transforming into hcp and fcc structures in the orientation relationships determined by RHEED, respectively.

Figure 15(a) shows the magnetization curves of 10-nm-thick bcc Fe[111] single-crystal film measured by applying the magnetic field along GaAs[112], GaAs[101], GaAs[211], GaAs[110], GaAs[121], or GaAs[011]. The magnetization curves are almost isotropic in the in-plane measurements. The easy magnetization axes of bcc[100], bcc[010], and bcc[001] are not parallel to the substrate surface but 35° canted from the substrate surface. Therefore, the effective easy magnetization directions are considered to be observed along bcc[211],

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**Fig. 13** (a)–(c) Pole-figure XRD patterns measured of (a) Fe, (b) Co, and (c) Ni films of 40 nm thickness prepared on GaAs(111) substrates measured by fixing the diffraction angle of 2θB at 47.5°, where signals with the intensities smaller than 10 cps are subtracted. (d), (e) Schematic diagrams of diffraction patterns simulated for (d) GaAs(111) substrate and (e) hcp crystals transformed from bcc structure in the crystallographic orientation relationships determined by RHEED.

**Fig. 14** (a)–(c) Pole-figure XRD patterns of (a) Fe, (b) Co, and (c) Ni films of 40 nm thickness prepared on GaAs(111) substrates measured by fixing the diffraction angle of 2θB at 51.8°, where signals with the intensities smaller than (a-1)–(c-1) 1 and (a-2)–(c-2) 10 cps are subtracted. (d), (e) Schematic diagrams of diffraction patterns simulated for (d) GaAs(111) substrate and (e) fcc crystals transformed from bcc structure in the crystallographic orientation relationships determined by RHEED.
Co, and (c) Ni films of 10 nm thickness prepared on GaAs(111) substrates. Crystals, show almost isotropic magnetic properties. The magnetization curves measured for Co and Ni films of no overcoat, possibly due to surface oxidation of the film sample with the thickness in a range from 1 to 40 nm. Nucleation of crystal with metastable structure and phase transformation process into stable structure are investigated by RHEED and XRDs. bcc(111) single crystals are formed in the early stages of film growth of not only Fe but also Co and Ni. The metastable structure is stabilized for Co and Ni films through hetero-epitaxial growth on GaAs(111) substrate. With increasing the thickness beyond 2 nm, the bcc-Co and the bcc-Ni crystals, respectively, start to transform into hcp and fcc structures through atomic displacements in the bcc(110), bcc(101) and bcc(011) close-packed planes.

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