Preparation and Structure Characterization of Sm-Ni Alloy Epitaxial Thin Films

Yusuke Hotta, Takato Yanagawa, Makoto Yamada, Mitsuru Ohtake, Masaaki Futamoto, Fumiyoshi Kirino*, and Nobuyuki Inaba**

Faculty of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan
*Graduate School of Fine Arts, Tokyo University of the Arts, 12-8 Ueno-Koen, Taito-ku, Tokyo 110-8714, Japan
**Faculty of Engineering, Yamagata University, 4-3-16 Jyounan, Yonezawa 992-8510, Japan

Sm\textsubscript{100–x}Ni\textsubscript{x} (at. %) alloy thin films are prepared on Cr(100) underlayers hetero-epitaxially grown on MgO(100) single-crystal substrates at 500 °C by employing an ultra-high vacuum molecular beam epitaxy system with varying the Sm content from Ni-rich to Sm-rich region (x = 10–25 at. %) including the SmNi\textsubscript{5} stoichiometry. The influence of film composition on ordered phase formation is studied by reflection high-energy electron diffraction and X-ray diffraction. Sm-Ni films with Sm compositions between 13 and 17 at. % consist of (112)\textsubscript{0} epitaxial crystals with RT\textsubscript{5} type structure. The epitaxial films involve two types of (1120) variant whose c-axes are lying in the film plane and rotated around the film normal by 90° each other. As the Sm content departs from the compositional range, an amorphous phase tends to be included in the film in addition to SmNi\textsubscript{5} ordered phase.

Key words: SmNi\textsubscript{5} ordered alloy thin film, epitaxial growth, rare earth permanent magnet, molecular beam epitaxy

1. Introduction

Magnetic thin films with the uniaxial magnetocrystalline anisotropy energy (K\textsubscript{u}) greater than 10\textsuperscript{7} erg/cm\textsuperscript{3} and with the easy magnetization axis parallel to the substrate surface have been investigated for nanocomposite magnets. In order to control the easy magnetization direction, well-defined epitaxial films are useful, since the crystallographic orientation of film can be controlled by that of single-crystal substrate. A bulk SmCo\textsubscript{5} ordered alloy crystal with RT\textsubscript{5}-type structure (R: rare earth metal, T: transition metal) shows K\textsubscript{u} of 1.1 × 10\textsuperscript{7} erg/cm\textsuperscript{3} along the c-axis\textsuperscript{1}. SmCo\textsubscript{5}(1120) and (1100) epitaxial films with the c-axis lying in the film plane have been respectively prepared on MgO single-crystal substrates of (100)\textsubscript{2–5} and (110)\textsubscript{1–6} orientations by employing W\textsuperscript{4}, Cr\textsuperscript{2,3}, and Fe\textsuperscript{5,6} underlayers. There is, however, a possibility that multiple hexagonal crystallographic phases such as RT\textsubscript{5}, RT\textsubscript{7}, and RT\textsubscript{3} are involved in addition to RT\textsubscript{5} phase\textsuperscript{7}. Conventional out-of-plane and in-plane X-ray diffractions (XRDs) are not easy to distinguish these phases, since the lattice spacings are very similar. Reciprocal lattice map measurements like electron diffraction are useful for the phase identification. In our previous studies\textsuperscript{8–10}, SmCo\textsubscript{5} epitaxial films with the c-axis parallel and perpendicular to the substrate surface were respectively prepared on Cr(100) and Cu(111) underlayers by employing a molecular beam epitaxy (MBE) system equipped with a reflection high-energy electron diffraction (RHEED) facility. In\textit{situ} RHEED revealed the crystallographic property during film formation, which varied depending not only on the substrate temperature but also on the film thickness. The Sm and Co sites in SmCo\textsubscript{5} structure can be replaced with other R and T elements, respectively. The structural and magnetic properties vary depending on the combination of T and R elements. Epitaxial RC\textsubscript{5} (R = Pr, Nd, etc.) ordered alloy films have been prepared\textsuperscript{11,12}, whereas there are few reports on the formation of SmT\textsubscript{5} (T = Fe, Ni) ordered films\textsuperscript{13–15}. Ni (1455 °C) has a lower melting point than Co (1495 °C) or Fe (1536 °C). Atomic diffusion activity of metal element is sometimes related with the melting point which reflects the atomic binding force. Ni atoms are thus considered to diffuse more easily and to have a lower activation energy in forming the SmT\textsubscript{5} compound. In our previous studies\textsuperscript{8–10}, Sm\textsubscript{17}Co\textsubscript{83} and Sm\textsubscript{17}Ni\textsubscript{83} (at. %) films were deposited on Cr(100) underlayers with varying the substrate temperature from 100 to 500 °C. The Sm\textsubscript{17}Ni\textsubscript{83} material showed a lower crystallization temperature compared with that of Sm\textsubscript{17}Co\textsubscript{83} material. In the present study, Sm\textsubscript{100–x}Ni\textsubscript{x} films are deposited on Cr(100) underlayers at 500 °C with varying the Sm content, x, from 10 to 25 at. %. The effect of Sm/Ni composition on ordered phase formation in Sm-Ni film is investigated.

2. Experimental Procedure

Thin films were deposited on polished MgO(100) substrates at 500 °C by using an MBE system. The base pressures were lower than 7 × 10\textsuperscript{-9} Pa. Ni was evaporated by electron beam heating, while Sm and Cr were evaporated by using Knudsen cells. The purities were higher than 99.9% for all evaporation materials. The film layer structure was Sm\textsubscript{100–x}Ni\textsubscript{x}(20 nm)/Cr(20 nm)/MgO. Cr(100) single-crystal underlayers are prepared by hetero-epitaxial growth on MgO(100) substrates. The epitaxial orientation relationship of
Sm$_{25}$Ni$_{75}$ films on Cr(100) underlayers at 500 °C. The film thicknesses are (a-1)–(e-1) 5, (a-2)–(e-2) 10, (a-3)–(e-3) 15, and (a-4)–(e-4) 20 nm. The incident electron beam is parallel to Cr[011] (type B).

**Fig. 1** RHEED patterns observed during formation of (a) Sm$_{10}$Ni$_{90}$, (b) Sm$_{13}$Ni$_{87}$, (c) Sm$_{17}$Ni$_{83}$, (d) Sm$_{20}$Ni$_{80}$, and (e) Sm$_{25}$Ni$_{75}$ films on Cr(100) underlayers at 500 °C. The film thicknesses are (a-1)–(e-1) 5, (a-2)–(e-2) 10, (a-3)–(e-3) 15, and (a-4)–(e-4) 20 nm. The incident electron beam is parallel to Cr[011] (type B). Cr(100)[011] || MgO(0001) was determined by RHEED. Sm and Ni were co-deposited on the Cr underlayer. The deposition rates of Sm and Ni during film formation, which were monitored by using quartz oscillators, were kept at constant values. The composition of Sm-Ni film, x, was varied from Ni-rich to Sm-rich region (10–25 at. % Sm) including the SmNi$_5$ stoichiometry (17 at. % Sm) by adjusting the deposition rates of Sm and Ni. The composition was confirmed by energy dispersive X-ray spectroscopy and the errors were less than 2 at. % from the compositions which were calculated by considering the deposition rates of Sm and Ni.

The surface structure during film formation was studied by *in situ* RHEED. The film structure was investigated by 2θ/ω-scan out-of-plane and 2θ/θ-scan in-plane XRDs with Cu-Kα radiation (λ = 0.15418 nm). The magnetization curves were measured by vibrating sample magnetometry.

**3. Results and Discussion**

Figure 1 shows the RHEED patterns observed for Sm-Ni films deposited on Cr(100) underlayers. Here, the incident electron beam is parallel to Cr[011] (type B). When the atomic arrangements of Cr(100) and Sm-Ni(1120) surfaces which respectively show four- and two-fold symmetries with respect to the perpendicular direction are considered, the Sm-Ni film is interpreted to epitaxially grow on the Cr underlayer in the orientation relationships of Sm-Ni(1120)[1100] || Cr(100)[011] (type A), Sm-Ni(1120)[0001] || Cr(100)[011] (type B). The diffraction patterns of Sm-Ni(1120) surfaces with $R_2T_{17}^*$, $RT_5^*$, $R_2T_7^*$, and $RT_1^*$-type structures simulated...
Fig. 3 (a-1)–(e-1) Out-of-plane and (a-2)–(e-2) in-plane XRD patterns of (a) Sm10Ni90, (b) Sm13Ni87, (c) Sm17Ni83, (d) Sm20Ni80, and (e) Sm25Ni75 films deposited on Cr(100) underlayers at 500 °C. The scattering vector of in-plane XRD is parallel to MgO[001]. The intensity is shown in logarithmic scale.

by making the incident electron beam parallel to [1100] are shown in Figs. 2(a-1)–(d-1), whereas those of Sm-Ni(1120) surfaces calculated by making the incident beam parallel to [0001] are shown in Figs. 2(a-2)–(d-2). When the surface structure of Sm-Ni(1120) film formed on Cr(100) underlayer is observed by RHEED, the overlapped diffraction patterns of Figs. 2(a-3)–(d-3) are thus expected to appear.

Figures 1(b-1) and (c-1) show the RHEED patterns observed for 5-nm-thick Sm-Ni films with the Sm contents of 13 and 17 at. %, respectively. The RHEED patterns are matching with the simulated diffraction pattern from RT5(1120) surface shown in Fig. 2(b-3) and are different from any of (1120) surfaces of R2T7-, R2T17-, and RT3-type structures depicted in Figs. 2(a-3), (c-3), and (d-3). Sm-Ni epitaxial films with RT5 ordered phase are obtained with the Sm contents of 13 and 17 at. %. The epitaxial orientation relationship is thus determined as

\[
\text{SmNi}_5(1120) || \text{Cr}(100)[011] \quad \text{(type A).}
\]

\[
\text{SmNi}_5(1120) || \text{Cr}(100)[0001] \quad \text{(type B).}
\]

The films consist of two (1120) variants whose c-axes are lying in the film plane and rotated around the film normal by 90° each other. In this configuration, the lattice mismatches at the SmNi5/Cr interface along SmNi5[1 1 0 0] and SmNi5[0001] are respectively calculated to be +5.0% and −2.4%, where the lattice constants of bulk SmNi5 (\(a = 0.4926\) nm, \(c = 0.3980\) nm\(^{17}\)) and Cr (\(a = 0.2884\) nm\(^{19}\)) crystals are used. Although there exists such a large misfit of +5.0% along SmNi5[1 1 0 0], epitaxial growth of SmNi5 crystal is taking place on Cr(100) underlayer. With increasing the thickness from 5 to 20 nm [Figs. 1(b-2)–(b-4), (c-2)–(c-4)], the sharpness of RHEED pattern gradually increases. The result suggests that the film strain caused by lattice mismatch around the Sm-Ni/Cr interface gradually decreases with increasing the thickness for the Sm13Ni87 and the Sm17Ni83 samples.

Figures 1(d) and (e) show the RHEED patterns observed for Sm-Ni films with \(x = 20\) and 25 at. %, respectively. Diffuse diffraction patterns are overlapped with the pattern from RT5(1120) epitaxial bicrystalline surface [Fig. 2(b-3)]. The reflection from RT5(1120) surface is far weaker for the Sm20Ni75 sample compared with that of Sm15Ni80 sample, due to an overlap with stronger diffuse reflection which originates from an amorphous structure. The result shows that these films consist of RT5 ordered phase mixed with amorphous phase and that the amorphous volume ratio increases with increasing the Sm composition. Figure 1(a) shows the RHEED patterns observed during the growth process of Sm-Ni film with Sm content of 10 at. %. Although no clear reflection is observed in the early stage up to 5 nm thickness [Fig. 1(a-1)], spotty and ring-shaped reflections start to be observed when the thickness is further increased as shown in Figs. 1(a-2)–(a-4). The 20-nm-thick film is considered to be consisting of epitaxial, poly-crystalline, and amorphous
phases. However it is risky to identify the crystal structure only from the RHEED data, though some of the RHEED spots coincide with those from RT \( (11 \overline{2}0) \) bicrystalline surface. The prepared thin film samples are then observed by using XRD techniques.

Figures 3(a–1)–(e–1) show the out-of-plane XRD patterns of Sm–Ni films with different Sm compositions. SmNi\(_5\) \( (11 \overline{2} 0) \) and SmNi\(_5\) \( (22 \overline{4} 0) \) reflections are recognized for all the films. It is made clear that the Sm\(_{50}\)Ni\(_{50}\) film involves epitaxial \( (11 \overline{2} 0) \) bicrystal. The XRD and RHEED indicate that SmNi\(_5\) phase is stabilized around the SmNi\(_5\) stoichiometry (Sm composition of 17 at. %) and amorphous phase tends to be included in a larger volume as the Sm composition shifts further from the stoichiometry. The values of full width at half maximum of \( \omega \)-scan rocking curves, \( \Delta \theta_0 \), of Sm–Ni films with the Sm contents of 10, 13, 17, 20, and 25 at. % measured by fixing the diffraction angle of \( 2 \theta \) at the peak angles of SmNi\(_5\)\( (11 \overline{2} 0) \) reflections were 3.6°, 3.2°, 2.7°, 3.9°, and 4.4°, respectively. The film strain is shown to become minimum at the stoichiometric composition.

Figures 3(a–2)–(e–2) show the in-plane XRD patterns measured by making the scattering vector parallel to MgO[001]. SmNi\(_{5}\)\( (0001) \), SmNi\(_{5}\)\( (0002) \), and SmNi\(_{5}\)\( (3300) \) reflections are observed. The in-plane XRD confirms the epitaxial orientation relationship with the Cr underlayer which was determined by RHEED. Figures 4(a) and (b) show the lattice parameters, \( a = 2d_{\text{SmNi}_{5}(11 \overline{2} 0)} \) and \( c = d_{\text{SmNi}_{5}(0001)} \), of Sm–Ni films estimated from the XRD data. It should be noted that the accuracies in \( \Delta \theta_0 \) estimated from the XRD data. It should be noted that the accuracies in the Sm content are high compared with the other films, similar to the case of c values. The \( \Delta \theta_0 \) values of films with x of 10, 13, 17, 20, and 25 at. % are 0.30, 0.72, 0.75, 0.65, and 0.32, respectively. The film with stoichiometric composition shows the highest \( \Delta \theta_0 \) value.

Figure 4(c) shows the compositional dependence of \( S \) value. The accuracies in \( \Delta \theta_0 \) values of Sm\(_{10}\)Ni\(_{89}\) and Sm\(_{25}\)Ni\(_{75}\) films are not so high compared with the other films, similar to the case of c values. The \( \Delta \theta_0 \) values of films with x of 10, 13, 17, 20, and 25 at. % are 0.30, 0.32, 0.72, 0.75, 0.65, and 0.32, respectively. The film with stoichiometric composition shows the highest \( \Delta \theta_0 \) value.

Figures 5 shows the magnetization curves of Sm\(_{17}\)Ni\(_{83}\)/Cr/MgO(100) specimens measured by applying the magnetic field along MgO[001] and MgO[011]. Here, MgO[001] is perpendicular to the c-axis of A-type SmNi\(_5\) variant and parallel to the c-axis of B-type variant. On the contrary, MgO[011] is the direction 45° rotated from the c-axis of each variant. The film shows an almost isotropic magnetic property.
4. Conclusion

Sm-Ni thin films are prepared on Cr(100) underlayers at 500 °C with varying the Sm content from 10 to 25 at. %. The effect of Sm/Ni composition on ordered phase formation is investigated. Sm-Ni(112_0) epitaxial films with RT5 ordered structure are obtained for the investigated compositional range. The epitaxial films with ordered phase consist of two types of (112_0) variant whose c-axes are lying in the film plane and rotated around the film normal by 90° each other. When the Sm composition shifts from around the stoichiometric composition, an amorphous phase tends to be included in the film in addition to SmNi 5 ordered phase. The lattice constants, a and c, increase as the Sm composition increases. The film with stoichiometric composition shows the highest S value (0.75).

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