Preparation of hcp-Ni(1120) Epitaxial Thin Films on Au(100) Single-Crystal Underlayers

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Abstract. Ni epitaxial films with an hcp structure are successfully obtained on Au(100) single-crystal underlayers formed on MgO(100) substrates at temperatures lower than 300 °C by molecular beam epitaxy. With increasing the substrate temperature, the volume ratio of more stable fcc phase increases in the film. The Ni film prepared at 100 °C consists primarily of hcp crystal with the (1120) plane parallel to the substrate surface coexisting with a small amount of fcc–Ni(100) crystal. The lattice constant of hcp–Ni crystal is determined as $a=0.249$ nm, $c=0.398$ nm, and $c/a=1.60$.

1. Introduction
$3d$ ferromagnetic transition metals have been widely studied for applications like magnetic recording media, magnetic heads, etc. Ni is a transition metal which crystallizes with an fcc structure in the bulk phase diagram. Preparations of hcp–Ni crystal, which is metastable and does not appear in the bulk phase diagram, have been reported in the forms of nano-particles and thin films [1]–[3]. Recently, epitaxial thin film growth has made possible to prepare metastable structures. hcp–Ni epitaxial film formation was observed in a very early stage of Ni film growth on MgO(100) substrate [4, 5]. However, the hcp phase transformed into more stable fcc phase upon further film deposition through atomic rearrangement [6]. In the present study, hcp–Ni epitaxial films were successfully prepared on Au(100) single-crystal underlayers. The X-ray diffraction (XRD) measured for 40-nm-thick Ni films showed that the films consist of hcp–Ni(1120) crystal. The structural and magnetic properties of metastable hcp–Ni films are reported.

2. Experimental procedure
Thin films were prepared on polished MgO(100) single-crystal substrates by using a molecular beam epitaxy (MBE) chamber with base pressures lower than $3\times10^{-8}$ Pa. Pure Ni (99.99%) and Cr (99.99%) were evaporated by electron beam heating, while pure Au (99.99%) was evaporated by using a Knudsen cell. The evaporation rate was kept constant at 0.01 nm/s for all materials. The film layer structure was Ni(40 nm)/Au(10 nm)/Cr(2 nm)/MgO(100). Substrates were heated at 500 °C for 1 hour in the UHV chamber to obtain clean surfaces. A 2-nm-thick Cr seed layer and a 10-nm-thick Au underlayer were sequentially deposited on the MgO substrate at 100 °C. Then, the sample was annealed at 500 °C for 1 hour to obtain a high-quality Au(100) single-crystal underlayer with flat
The hcp–Ni crystal is determined from the Ni(1120) XRD peak to be 0.249 nm. The lattice constant, \(a\), of the hcp–Ni crystal is determined from the Ni(1120) XRD peak to be 0.249 nm. The lattice constant, \(c\), of the hcp–Ni crystal is 0.17 nm. The flatness examined by atomic force microscopy was 0.17 nm in rms roughness. The epitaxial orientation relationship of Au(100)[001] || Cr(100)[011] || MgO(100)[001] was determined from the reflection high energy electron diffraction (RHEED) observation. A 40-nm-thick Ni layer was deposited on the Au underlayer at a substrate temperature ranging between 100 and 500 °C. For the Ni layers prepared at 100 and 200 °C, the RHEED intensity from fcc–Ni crystal increases, whereas that from hcp–Ni crystal decreases. For the Ni layers prepared at 400 and 500 °C, a diffraction pattern of only the fcc–Ni crystal is observed. The epitaxial orientation relationship of Au(100)[001] || MgO(100)[001] was investigated by out-of-plane (2θ–ω–scan), in-plane (2θ/ϕ–scan), and ϕ–scan XRD with Cu–Kα radiation (\(λ=0.14518\) nm). The magnetization curves were measured by using a vibrating sample magnetometer.

3. Results and discussion

Ni epitaxial thin films were obtained on Au(100) single-crystal underlayers. Figure 1 shows the RHEED patterns observed during Ni deposition on Au(100) underlayers heated at different temperatures. For the Ni layers prepared at 100 and 200 °C, in-situ RHEED observation shows that a clear diffraction pattern of hcp–Ni(1120) reflection starts to be observed from the beginning of Ni deposition and it remains unchanged during Ni layer formation (figure 1(a)). The epitaxial orientation relationships of Ni(11 \( \overline{2} \) 0)[0001] \(_{\text{hcp}}\) || Au(100)[001] \(_{\text{fcc}}\) (Type A) and Ni(11 \( \overline{2} \) 0)[110] \(_{\text{hcp}}\) || Au(100)[001] \(_{\text{fcc}}\) (Type B) are determined by the RHEED observation. The hcp–Ni crystal consists of two types of (1120) domains whose orientations are rotated around the film normal by 90° each other. In the early stage of Ni layer growth at 300 °C, two kinds of RHEED patterns, hcp–Ni(1120) and fcc–Ni(100), are overlapped, as shown in figure 1(b). The orientation relationship between the fcc–Ni(100) crystal and the Au(100) underlayer is Ni(100)[001] \(_{\text{fcc}}\) || Au(100)[001] \(_{\text{fcc}}\). With increasing the layer thickness, the RHEED intensity from fcc–Ni crystal increases, whereas that from hcp–Ni crystal decreases. For the Ni layers prepared at 400 and 500 °C, a diffraction pattern of only the fcc–Ni(100) reflection is observed throughout the course of Ni deposition, as shown in figure 1(c). The hcp–Ni phase is considered to be stable on the Au(100) underlayer at temperatures lower than 300 °C, similar to the case of hcp–Ni powder where hcp–Ni phase transformed into more stable fcc–Ni phase at a temperature higher than 380 °C [2].

Figure 2 shows the out-of-plane and the in-plane XRD spectra of Ni films measured after film deposition. For the Ni layers prepared at temperatures between 100 and 300 °C, Ni(1120) out-of-plane, Ni(1100) in-plane, and Ni(0002) in-plane XRD peaks are clearly recognized. The lattice constant, \(a\), of the hcp–Ni crystal is determined from the Ni(1120) XRD peak to be 0.249 nm. The lattice constant, \(c\), of the
reflections vary depending on the incident X-ray angle, prepared at 500 and 200 °C, respectively. The intensities of Au(002), hcp–Ni(0002), and fcc–Ni(002) increase, suggesting that the volume ratio of hcp crystal decreases, whereas that of fcc crystal increases, as expected from the RHEED observations. In order to study the distribution of fcc crystal transformed through atomic rearrangement. The orientation relationships between the hcp–Ni and the fcc–Ni crystals investigated by φ–scan XRD analysis (figure 4) are Ni(1120)[0001]_{hcp} || Ni(100)[001]_{fcc} (Type A′) and Ni(1120)[1100]_{hcp} || Ni(100)[001]_{fcc} (Type B′). With increasing the substrate temperature, the XRD intensity from hcp–Ni crystal decreases, whereas from fcc–Ni crystal increases, suggesting that the volume ratio of hcp crystal decreases, whereas that of fcc crystal increases. The layer prepared at 100 °C consists primarily of hcp crystal coexisting with a small amount of fcc crystal. At temperatures higher than 400 °C, fcc–Ni(100) single-crystal films are formed, as expected from the RHEED observations. In order to study the distribution of fcc crystal transformed from hcp crystal along the film thickness direction, in-plane XRD analysis was performed by changing the incident X-ray angle [7]. Figures 5(a) and 5(b) show the in-plane XRD spectra of Ni layers prepared at 500 and 200 °C, respectively. The intensities of Au(002), hcp–Ni(0002), and fcc–Ni(002) reflections vary depending on the incident X-ray angle, φ. Incident X-ray angle dependence on intensity is shown in figures 5(c)–5(f). For the layer prepared at 200 °C, the peak value of hcp–Ni reflection is smaller than that of fcc–Ni reflection, which suggests that large volume of hcp–Ni crystal is calculated from the lattice constant, a, and the lattice spacing, d_{Ni(1101)}, to be 0.398 nm, by considering the structure shown in figure 3. The c/a value is thus 1.60. Although the RHEED observation shows only the reflection of hcp–Ni crystal for the Ni layers prepared at 100 and 200 °C, Ni(200)_{fcc} out-of-plane and Ni(002)_{fcc} in-plane XRD peaks are also observed. The result suggests that parts of the hcp–Ni crystal have transformed into more stable fcc–Ni crystal during the film growth process through atomic rearrangement. The orientation relationships between the hcp–Ni and the fcc–Ni crystals investigated by φ–scan XRD analysis (figure 4) are Ni(1120)[0001]_{hcp} || Ni(100)[001]_{fcc} (Type A′) and Ni(1120)[1100]_{hcp} || Ni(100)[001]_{fcc} (Type B′). With increasing the substrate temperature, the XRD intensity from hcp–Ni crystal decreases, whereas from fcc–Ni crystal increases, suggesting that the volume ratio of hcp crystal decreases, whereas that of fcc crystal increases. The layer prepared at 100 °C consists primarily of hcp crystal coexisting with a small amount of fcc crystal. 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exists near the layer surface, whereas fcc–Ni crystal tends to exist preferentially near the Au underlayer interface. These experimental results indicate a possibility that the hcp–Ni crystal begins to transform into more stable fcc–Ni crystal in the Ni layer.

The magnetization curves of Ni layers prepared at 100 and 400 °C are shown in figure 6. The saturation magnetization values are similar to that of bulk fcc–Ni crystal for both samples. These layers are easily magnetized when the magnetic field is applied along the MgO[011] direction, whereas the magnetization curves measured along the MgO[001] direction saturate at higher applied fields. The anisotropy field of Ni layer prepared at 100 °C, where the XRD result suggests that the layer consists primarily of hcp crystal, is about 3.5 times higher than that of fcc–Ni(100) single-crystal layer prepared at 400 °C. These behaviors are similar to the cases of hcp–Co(1120) epitaxial bicrystalline films grown on MgO(100) substrate [8] and fcc–Co(100) single-crystal films grown on SrTiO3(100) substrate [9]. The higher anisotropy field of Ni layer prepared at 100 C is considered to agree with the magnetic behavior of hcp–Ni crystal predicted by a theoretical calculation that ferromagnetic hcp–Ni is similar to ferromagnetic hcp–Co [10].

However, in order to determine the accurate value of magnetic anisotropy constant of hcp–Ni crystal, it is necessary to prepare an hcp–Ni single-crystal film which is consisting of only hcp–phase. The Ni epitaxial thin films prepared in the present study include small amount of fcc phase as shown by the XRD analysis. It seems possible to prepare pure hcp–Ni epitaxial thin films by improving the film growth condition, for example, by further lowering the substrate temperature below 100 °C.

4. Conclusion

Ni(1120) epitaxial films with an hcp structure are successfully obtained on Au(100) single-crystal underlayers formed on MgO(100) substrates at temperatures lower than 300 °C. The hcp crystal consists of two types of domains whose orientations are rotated around the film normal by 90° each other. Some volume of the hcp–Ni crystal transforms into more stable fcc–Ni phase during film growth process through atomic rearrangement inside the Ni layer. With increasing the substrate temperature, the volume ratio of hcp crystal decreases, whereas that of fcc crystal increases. The magnetic properties of Ni film prepared at 100 °C reflect those of hcp–Ni crystal.

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