Preparation of Co(0001)$_{hcp}$ and (111)$_{fcc}$ Films on Single-Crystal Oxide Substrates

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Abstract. Co thin films were prepared on oxide single-crystal substrates of Al$_2$O$_3$(0001)$_{051}$, MgO(111)$_{B1}$, and SrTiO$_3$(111)$_{E21}$ by ultra high vacuum molecular beam epitaxy. Effects of substrate material and substrate temperate on the film growth and the crystallographic properties were investigated. Co epitaxial thin films of hcp(0001) and/or fcc(111) orientations are obtained on all the substrate. With increasing the substrate temperature, the volume ratio of hcp to fcc increases for the Co films grown on Al$_2$O$_3$ and MgO substrates, whereas the ratio decrease for the Co film grown on SrTiO$_3$ substrate. The in-plane lattice strain is larger than the out-of-plane strain due to accommodation of lattice mismatch between the film and the substrate.

1. Introduction
Magnetic thin films with perpendicular magnetic anisotropy have been investigated for applications like magnetic recording media, magnetic random access memory devices, etc. Co has two stable crystallographic phases, hcp and fcc. Co-based alloy thin films with hcp structure and multilayer films combined with thin fcc–Co and noble metal (Pd, Pt, etc.) layers have been frequently used for such applications. These are mostly hcp(0001) or fcc(111) oriented polycrystalline films. The films generally include stacking faults existing parallel to the closed packed plane and even small volume of crystals with other orientations. The crystallographic quality gives strong influences on the magnetic properties like magnetic anisotropy [1], Gilbert’s damping constant [2], etc. Well-defined epitaxial thin films are strong candidates for future magnetic applications [3, 4], since the film uniformity and the magnetic anisotropy are well controlled. Epitaxial films are also useful to investigate the basic structural and magnetic properties. Co(0001)$_{hcp}$ single-crystal films have been prepared by employing underlayers such as Au(111)$_{fcc}$ [3], Ti(0001)$_{hcp}$ [5], and Ru(0001)$_{hcp}$ [6], whereas Co(111)$_{fcc}$ thin films epitaxially grow on Cu(111) underlayers [7]. However, the epitaxial film structure delicately varies depending on the deposition condition like substrate material, substrate temperature, etc. Oxide single-crystal substrates generally offer stable surface structures. In the present study, Co thin films were prepared on three kinds of oxide single-crystal substrates under similar experimental conditions to investigate the effects of substrate material and substrate temperature on the film growth and the structure. The detailed film structures were investigated by in-situ reflection high energy electron diffraction (RHEED) and ex-situ X-ray diffraction (XRD).

2. Experimental procedure
Co thin films of 40 nm thickness were deposited on polished Al$_2$O$_3$(0001)$_{051}$, MgO(111)$_{B1}$, and SrTiO$_3$(111)$_{E21}$ substrates at temperatures ranging between 100 and 500 °C by using a molecular beam
epitaxy chamber with base pressures lower than $3 \times 10^{-8}$ Pa. Substrates were heated at 500 °C for 1 hour in the ultra high vacuum chamber to obtain clean surfaces. The surface structure was checked by RHEED. The RHEED patterns observed for the substrates correspond to those from clean surfaces, as shown in figures 1(a), 3(a), and 5(a). Pure Co (99.99%) was evaporated by electron beam heating. The deposition rate was kept constant at 0.01 nm/s.

The surface structure during Co deposition was studied by in-situ RHEED. The film structure was investigated by out-of-plane ($2\theta$–$\omega$–scan), in-plane ($2\theta$–$2\theta$–$\phi$–scan), and pole figure XRD with Cu–$K\alpha$ radiation ($\lambda$=0.15418 nm). The cross-sectional microstructure was observed by transmission electron microscopy.

3. Results and discussion

Co epitaxial thin films with closed packed planes parallel to the substrate surfaces were obtained on Al$_2$O$_3$(0001)$_{DyS}$ and MgO(111)$_{B}$ substrates for the investigated substrate temperatures. On SrTiO$_3$(111)$_{E}$ substrates, Co epitaxial thin films were formed at temperatures higher than 300 °C, whereas Co polycrystalline films grew at temperatures lower than 200 °C. Figures 1(c)–(f) show the RHEED patterns observed during Co deposition on Al$_2$O$_3$(0001)$_{DyS}$ substrates heated at different temperatures. Clear RHEED patterns start to be observed from the beginning of Co deposition and they remain unchanged during 40-nm-thick Co film formation. With increasing the substrate temperature, the diffraction spots and streaks become sharper, which indicates that the strain in the film decreases further by employing high substrate temperatures. For the films prepared at 100 and 200 °C [figures 1(c) and (d)], the RHEED pattern consists of spots corresponding to fcc(111) texture [figure 1(g)] and streaks along the fcc[111] direction. The fcc(111) pattern consists of two reflections, as shown by the spots, A and B, in the RHEED spot maps of figure 1(g). The streaks indicate that the film has atomically flat terraces and a possibility of including hcp(0001) crystals. For the films prepared at temperatures higher than 300 °C [figures 1(e) and (f)], the RHEED spots are not recognized but only the streaks along the fcc[111] and/or the hcp[0001] direction are observed. The

![Figure 1](image1)

**Figure 1.** RHEED patterns observed for (a) an Al$_2$O$_3$(0001)$_{DyS}$ substrate and (c)–(f) Co films grown on Al$_2$O$_3$ substrates at (c) 100 °C, (d) 200 °C, (e) 300 °C and (d) 500 °C. The film thicknesses are [(c–1),(d–1),(e–1),(f–1)] 2 nm and [(c–2),(d–2), (e–2),(f–2)] 40 nm. RHEED spot maps of (b) $D_{11}$, (g) fcc(111), and (h) hcp(0001). The incident electron beam is parallel to the Al$_2$O$_3$(1100)$_{DyS}$ direction.

![Figure 2](image2)

**Figure 2.** Epitaxial orientation relationships of (a) Co(111)$_{hcp}$ $\parallel$ Al$_2$O$_3$(0001)$_{DyS}$ and (b) Co(0001)$_{hcp}$ $\parallel$ Al$_2$O$_3$(0001)$_{DyS}$. 
epitaxial orientation relationships of the fcc and the hcp crystals with respect to the substrate are respectively determined by RHEED to be Co(111)[1 1 0]_{fcc} (Type A) (Type B) || Al_{2}O_{3}(0001)[1 1 0]_{D_51} and Co(0001)[1 1 0]_{hcp} || Al_{2}O_{3}(0001)[1 1 0]_{D_51}. The fcc–Co crystal has two kinds of epitaxial orientation relationships with respective to the substrate [figure 2(a)], whereas the hcp–Co crystal has one orientation relationship [figure 2(b)]. The orientations of two types of fcc(111) variants are rotated around the film normal by 180 degree each other. Al_{2}O_{3} crystal has D_51 crystal structure and the Al_{2}O_{3}(0001) consists of two alternate layers of Al and O. The atomic arrangements of Al and O layers are rotated around the film normal by 30 degrees each other. When the structure of Al_{2}O_{3} is considered, there are two possibilities of Co crystal nucleation on Al_{2}O_{3}(0001)_{D_51}. One possibility is that Co atoms of fcc(111) or hcp(0001) fit with the Al atoms of Al_{2}O_{3}(000 1_{odd}), where the lattice mismatch is calculated to be 5.6% (| (2a_{fcc-Co}/2^{1/2} - a_{Al2O3})/a_{Al2O3} | = 5.6%, | (2a_{hcp-Co} - a_{Al2O3} | = 5.6%). Another possibility is that Co atoms fit with the O atoms of Al_{2}O_{3}(000 1_{even}), where the mismatch increases up to 8.9% ( | (2a_{fcc-Co}/2^{1/2} - a_{Al2O3}/3^{1/2})/a_{Al2O3} | = 8.9%, | (2a_{hcp-Co} - a_{Al2O3}/3^{1/2})/a_{Al2O3} | = 8.9%). The experimental result shows that the arrangement of Co atoms is similar to that of O atoms, as shown in figure 2. A theoretical simulation supports that 3d ferromagnetic transition metal film growth on Al_{2}O_{3} substrate is strongly influenced by the O atoms located on the substrate surface [8]. The Co film growth on Al_{2}O_{3}(0001)_{D_51} is considered to be influenced by the atomic arrangement of O atoms of Al_{2}O_{3}. Furthermore, in the epitaxial orientation relationship, there exists a large mismatch of about 9% between the film and the substrate. However, clear RHEED patterns are observed throughout the course of Co deposition [figures 1(b)–(f)]. It is known that misfit dislocations are easily introduced in a film around the film/substrate to reduce the mismatch between immiscible elements when a weak binding force works between the deposited atoms and the substrate atoms. This type of epitaxial growth where misfit dislocations are introduced in the film around the interface is reported for the Cr/MgO [9] and the FeCo/MgO [10] systems. The epitaxial growth of Co films on Al_{2}O_{3}(0001)_{D_51} substrates is also considered to follow the growth mode. Figure 3 shows the high-resolution cross-sectional TEM image of a Co film grown on Al_{2}O_{3}(0001)_{D_51} substrate at 500 °C. A sharp boundary is recognized between the film and the substrate, where misfit dislocations are considered to be introduced so as to reduce the lattice mismatch existing at the Co/Al_{2}O_{3} interface.

Similar tendency of film growth was recognized for the Co thin films formed on MgO(111)_{B1} substrates. Figure 4 shows the RHEED patterns observed during Co deposition on MgO(111)_{B1} substrates heated at different temperatures. Clear diffraction patterns corresponding to fcc(111) and/or hcp(0001) texture are observed throughout the course of Co deposition. The RHEED patterns observed for films prepared at 100 and 200 °C [figures 4(c) and (d)] consist of fcc(111) diffraction spots and the streaks along the fcc[1 1 1] direction, whereas those observed for films prepared at temperatures higher than 300 °C [figures 4(e) and (f)] consist of only the streaks. The epitaxial orientation relationships of Co(111)[1 1 0]_{fcc} (Type A) (Type B) || MgO(111)[1 1 0]_{B1} and Co(0001)[1 1 2]_{hcp} || MgO(111)[1 1 0]_{B1} are determined by RHEED. MgO crystal has B1 structure and the MgO(111)_{B1} consists of two alternate layers of Mg and O. The atomic arrangement of O atoms located on the substrate surface is same as that of Mg atoms. The arrangement of Co atoms is also similar to those of O and Mg, as shown in figure 5. On MgO(111) substrates, the Co film growth is also considered to be influenced by the atomic arrangement of O atoms of MgO. Furthermore, there exists a fairly large mismatch of about 16% ( | (a_{fcc-Co}/2^{1/2} - a_{MgO}/2^{1/2})/a_{MgO} | = 15.9%, | (a_{hcp-Co} - a_{MgO}/2^{1/2})/a_{MgO} | = 15.8%). Misfit dislocations are expected to be introduced in the films at the Co/MgO interfaces.

Figures 6(c)–(f) shows the RHEED patterns observed during Co deposition on SrTiO_{3}(111)_{E21} substrates heated at different temperatures. For the films prepared at 100 and 200 °C [figures 6(c) and
Figure 4. RHEED patterns observed for (a) an MgO(111) substrate and (c)-(f) Co films grown on MgO(111) substrates at (c) 100 °C, (d) 200 °C, (e) 300 °C and (d) 500 °C. The film thicknesses are [(c–1),(d–1),(e–1),(f–1)] 2 nm and [(c–2),(d–2),(e–2),(f–2)] 40 nm. (b) RHEED spot map of B1(111). The incident electron beam is parallel to the MgO(111) direction.

Figure 5. Epitaxial orientation relationships of (a) Co(111) || MgO(111) and (b) Co(0001) || MgO(111).

(d), the ring RHEED patterns typical for polycrystalline structure are observed throughout the course of Co deposition. For the film prepared at 300 °C, a diffuse RHEED pattern is observed in an early stage of Co film growth [figure 6(e–1)]. With increasing the film thickness, an overlap of the ring pattern and the pattern corresponding to fcc(111) and/or hcp(0001) texture appears [figure 6(e–2)]. Co thin films grown on SrTiO3(111) substrates are apparently strained. With increasing the substrate temperature [figure 6(f)], the diffraction pattern becomes sharper, which indicates that the strain in the film decreases by employing higher substrate temperatures. The epitaxial orientation relationships of Co(111)[112] || SrTiO3(111)[110] and Co(0001)[110] || SrTiO3(111)[100] are determined by RHEED. The lattice mismatch is calculated to be about 5% ([2aCo-fcc/2 - aSTO(3/2)/2] || [aSTO(3/2)/2] = 4.8%, [2ahcp-Co - aSTO(3/2)/2] || [aSTO(3/2)/2] = 4.9%). SrTiO3 has E21 structure and the SrTiO3(111)21 consists of two alternate layers. One layer consists of Sr and O atoms. Another layer consists of only Ti atoms. The atomic arrangement of Co film is rotated around the film normal by 30 degrees with respective to that of Sr–O layer. The Co film growth mode on SrTiO3(111) seems to be different with those on Al2O3(0001) and MgO(111).

In order to investigate the crystal structure of Co epitaxial films grown on oxide substrates, pole figure XRD analysis was performed. Figures 8(a)–(c) and (e)–(f) shows the pole figure XRD spectra of fcc–Co(111) and hcp–Co(110) measured by making the optical axes of XRD system shown in figures 8(d) and (h), respectively. For the films prepared on Al2O3(0001) and MgO(111) substrates at 100 °C, six reflections, which originate from the two types of fcc–Co(111) variants (Types A and B), are observed with 60 degrees separation for the spectra of fcc(111) poles [Figures...
of hcp to fcc crystal is apparently influenced by the substrate material and the substrate temperature. Therefore, the diffraction angle. The temperatures of 400 and 500 °C, strong fcc{111}\(\text{[figures 8(c) and (g)]}\), which indicates that the films consist primarily of fcc crystals. The volume ratio on the lattice constant, due to the increase in the ratio of fcc to hcp. Figure 10(b) shows the substrate temperature dependence in the volume ratio of hcp to fcc, whereas the temperature, the temperature, the c value of Co films grown on \(\text{Al}_2\text{O}_3\) and MgO substrates decrease due to the increase in the volume ratio of hcp to fcc, whereas the c value of Co film grown on SrTiO\(_3\) substrate increases due to the increase in the ratio of fcc to hcp. Figure 10(b) shows the substrate temperature dependence on the lattice constant, \(a\), estimated from the Co(222)\(\text{fcc}\) and/or (1120)\(\text{hcp}\) in-plane XRD peak diffraction angle. With increasing the substrate temperature, the c values of Co films grown on \(\text{Al}_2\text{O}_3\) and MgO substrates decrease due to the increase in the volume ratio of hcp to fcc, whereas the c value of Co film grown on SrTiO\(_3\) substrate increases due to the increase in the ratio of fcc to hcp. With increasing the substrate temperature, \(\Delta\theta_{90}\) and \(\Delta\theta_{50}\) decrease, indicating that the film strain decreases by employing higher substrate temperatures.

Figure 8. Pole figure XRD spectra of [(a),(b),(c)] Co{1\(\bar{1}\)1}\(\text{fcc}\) and [(e),(f),(g)] Co{1\(\bar{1}\)01} Co{1\(\bar{1}\)01} poles measured for Co films grown on [(a),(e)] \(\text{Al}_2\text{O}_3(0001)\)\(_{\text{polycrystalline}}\), [(b),(f)] MgO(111)_\text{bulk}, and [(c),(g)] SrTiO\(_3(111)_{\text{bulk}}\) substrates. The intensity is shown in a logarithmic scale. The symbols, A and B, respectively correspond to the epitaxial orientation relationship of Types A and B explained in the text. Schematic model showing the optical axes of pole figure XRD measurements for (d) Co{111}\(\text{fcc}\) and (h) Co{1\(\bar{1}\)01}\(\text{hcp}\) poles.

8(a) and (b)], whereas there are no reflections for the spectra of hcp{1\(\bar{1}\)01} poles [figures 8(e) and (f)]. This result show that the films consist of pure fcc{111} crystals. When the substrate temperature exceeds 200 °C, six-fold symmetrical reflections appear in the spectra of hcp{1\(\bar{1}\)01} poles [figures 8(a) and (b)]. The films consist primarily of fcc crystal and include very small amount of stacking faults (hcp crystals). With increasing the substrate temperature beyond 300 °C, the fcc-to-hcp volume ratio delicately varied depending on the substrate material. For the films prepared on \(\text{Al}_2\text{O}_3\) substrates at temperatures higher than 300 °C, strong hcp{1\(\bar{1}\)01} and weak fcc{111} reflections are observed [figures 8(a) and (e)]. The films consist primarily of hcp crystals coexisting with small amount of fcc crystals. For the films prepared on MgO substrates at temperatures higher than 300 °C, only the hcp{1\(\bar{1}\)01} reflections are observed, as shown in figures 8(b) and (f). The films consist of pure hcp crystals. On the other hand, for the Co films epitaxially grown on SrTiO\(_3(111)_{\text{bulk}}\) substrates at elevated temperatures of 400 and 500 °C, strong fcc{111} and weak hcp{1\(\bar{1}\)01} reflections are recognized [figures 8(c) and (g)], which indicates that the films consist primarily of fcc crystals. The volume ratio of hcp to fcc crystal is apparently influenced by the substrate material and the substrate temperature.

Figures 9(a) and (b) show the out-of-plane and the in-plane XRD spectra of Co films grown on \(\text{Al}_2\text{O}_3\), MgO, and SrTiO\(_3\) substrates at 600 °C. The Co(111)\(\text{fcc}\) and/or (0002)\(\text{hcp}\) out-of-plane and the Co(220)\(\text{fcc}\) and/or (1120)\(\text{hcp}\) in-plane XRD reflections are clearly observed for all the substrates. Figure 10(a) shows the substrate temperature dependence on the lattice constant, c, estimated from the Co(222)\(\text{fcc}\) and/or (0004)\(\text{hcp}\) out-of-plane XRD peak diffraction angle. With increasing the substrate temperature, the c values of Co films grown on \(\text{Al}_2\text{O}_3\) and MgO substrates decrease due to the increase in the volume ratio of hcp to fcc, whereas the c value of Co film grown on SrTiO\(_3\) substrate increases due to the increase in the ratio of fcc to hcp. Figure 10(b) shows the substrate temperature dependence on the lattice constant, \(a\), estimated from the Co(222)\(\text{fcc}\) and/or (1120)\(\text{hcp}\) in-plane XRD peak diffraction angle. The \(a\) value is almost constant for all samples due to accommodation of lattice mismatch between the film and the substrate. Therefore, the \(\Delta\theta_{90}\) value [figure 10(c)] is larger than the \(\Delta\theta_{50}\) value [figure 10(d)] for same substrate temperatures. With increasing the substrate temperature, \(\Delta\theta_{90}\) and \(\Delta\theta_{50}\) decrease, indicating that the film strain decreases by employing higher substrate temperatures.
Figure 9. (a) Out-of-plane and (b) in-plane XRD spectra of Co films grown on Al2O3(0001), MgO(111), and SrTiO3(111) substrates at 500 °C. The intensity is shown in a logarithmic scale. The arrows, $K\beta$ and WL, show the reflections caused by XRD with Cu–$K\beta$ and W–La radiations.

4. Conclusion
Co epitaxial thin films were obtained on Al2O3(0001)$_{21}$, MgO(111)$_{21}$, and SrTiO3(111)$_{21}$ substrates. The film growth and the crystallographic properties were investigated by in-situ RHEED and ex-situ XRD. Co epitaxial films consist of fcc(111) and/or hcp(0001) crystals. With increasing the substrate temperature, the volume ratio of hcp to fcc increases for the Co films grown on Al2O3 and MgO substrates, whereas the ratio of fcc to hcp increases for the Co film grown on SrTiO3 substrate. The lattice constant and the film strain are influenced by the substrate material and the substrate temperature.

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