Hcp Co Films Prepared by Low Kinetic Energy Sputtering

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Abstract—Polycrystalline Co films of hcp single phase were produced on glassy substrates by Gas-Flow-Sputtering technique. The hcp Co films were obtained at the substrate temperatures below 620 K and the mixture of hcp and fcc phases was formed above the temperature. Two kinds of preferred orientations of texture, where (00.1)hcp or (10.0)hcp plane was parallel to the film plane, were observed.

I. INTRODUCTION

Cobalt is a well-known example showing martensitic transformation at $T_M \approx 690$ K [1]. The hcp and fcc phases are stable below the $T_M$ and above the $T_M$ in bulk Co, respectively. However, the crystal structure of Co films prepared by physical vapor deposition (PVD) depends on the growth process and conditions [2 - 5]. Morawe et. al. [4] investigated structural dependence on the growth temperature for sputtering process. Gronckel et. al. [5] precisely studied MBE process for Co films and led similar results; that is, Co films of single hcp phase do not grow on glass substrates at any temperature and only grow on sapphire or mica with utilizing epitaxy growth. Mixture of hcp and fcc phases tends to be formed at low temperatures. As far as the authors know, there is no clear explanation why Co films of hcp single phase are not formed on the glass substrate maintained at the temperature lower than the martensitic transition temperature $T_M$.

Sputtered particles have large kinetic energy in the range of a few eV [6]. This energy corresponds to temperature of a few ten thousand Kelvin. On the other hand, thermally evaporated Co atoms in vacuum are estimated to have the energy nearly equal to the thermal energy at its boiling temperature (3143 K). In the film growth by using sputtering or thermal evaporation technique, such high energy atoms are deposited onto substrates. The film growth process from high temperature vapor is thought to be attributable to the formation of high temperature phase (fcc phase). The authors have assumed that hcp Co films would be produced if the substrate temperature is lower than $T_M$ and at the same time the kinetic energy of depositing atoms is less than the thermal energy at $T_M$. In this work, the structure and magnetic properties of Co films deposited by Gas-Flow-Sputtering (GFS) [7, 8] were investigated to prove our hypothesis. GFS is a sputter-deposition technique at a high pressure in the range of 1 Torr and allows the deposition of low kinetic energy atoms. A hollow cathode is used as the target through which Ar gas is streaming at a high speed from a few m/s to tens m/s. The sputtered atoms are completely thermalized by collisions with Ar gas and carried to the substrate by Ar gas flow. The energy of depositing atoms is equal to the thermal energy of Ar gas.

The results obtained has revealed that polycrystalline Co films of hcp single phase grow on glassy substrates at the substrate temperatures below 620 K and two kinds of crystallographic orientations of films can be controlled.

II. EXPERIMENT

Figure 1 shows the GFS apparatus used in this experiment. 99.9 % Co tube of 4 cm inner diameter and 6 cm length was used as the target. The substrate was placed at 8 cm apart from the target. The chamber was evacuated below $5 \times 10^{-7}$ Torr prior to deposition. 99.9999 pure Ar was introduced to the gas-inlet of the chamber after being purified through a getter type purifier (UrtraPure Systems PF-200), though the impurity concentration was not measured. During sputtering the Ar pressure was maintained at 1 Torr under the flow rate of 500 sccm. The DC hollow cathode discharge was carried out with an
electric power input of 470 W which led to a deposition rate of 0.1 nm/s. The substrate was heated with W heating coil from the backside and the temperature was monitored using a thermocouple. When the substrate was unheated, the temperature was raised up to 350 K in about 10 min and thereafter nearly settled to the value. Then the temperature of Ar gas impinging to the substrate was supposed not to be much higher than 350 K. The film structure was characterized by conventional x-ray diffraction (Cu-Kα radiation was used) and electron diffraction in conjunction with electron microscopy (TEM). A vibrating sample magnetometer (VSM) was used to measure the hysteresis loop of films at room temperature. Slideglass (MATSUNMI S-1111) or SiO₂ glass was used as the substrate for x-ray diffraction and VSM measurement, and carbon thin film coated on microgrids was used for TEM observation.

### III. RESULTS AND DISCUSSION

Figure 2 shows typical results of x-ray θ-2θ scans of 300-nm Co films grown on SiO₂ substrates at different substrate temperatures. All measurements were taken *ex situ* at room temperature. We can see the strong peak at 2θ ~ 44.5° which corresponds to the (111)fcc or (00.2)hcp Bragg peak [9] at substrate temperatures from 350 K to 670 K. For substrate temperatures below 470 K the weak peaks at 2θ = 41.7° and 98.7° which correspond to (10.0)hcp and (00.2)hcp peaks, respectively, were seen. This temperature dependence of the diffraction profiles suggests that hcp Co is formed below 470 K. The evolution of the peak at 2θ = 44.5° is assumed to be due to the development of a strong texture with the crystallographic orientation of (00.1) plane for hcp phase parallel to the film plane. We precisely investigated the temperature dependence of the Bragg peak at 2θ ~ 44.5° to obtain more detailed information about the phase transition. The peak position of the films deposited below 620 K agreed with that of (00.2)hcp at 2θ = 44.5° [5]. The peak intensity increased and was accompanied by a decrease in width with increasing the substrate temperature up to 620 K. However, it was observed that above 630 K the peak at 2θ = 44.5° was reduced and, at the same time, the peak corresponding to (111)hcp peak at 2θ = 44.2° started to be superimposed. In the region between 630 K and 670 K, the peak profiles with broad width suggested a mixture of the hcp (00.2) and fcc (111) d-spacings of the two structural modification of cobalt, maybe containing numerous stacking faults.

We also used electron diffraction to determine the crystal structure for thin Co films. Figure 3 shows the electron diffraction pattern of 50-nm film deposited without heating substrate. These measurements were carried out *ex situ* after taking the films out of the chamber. The strong Debey rings from hcp phase and weak ones from CoO were observed for 7 nm to 50 nm thick films. For thinner films the oxidation of films caused by the *ex situ* measurements inhibited the precise determination of the crystal structure of films. Figure 4 shows the electron diffraction pattern of 50-nm film deposited at 650 K. In this pattern the Debey rings corresponding to the mixed phases of hcp Co and fcc Co are seen. These structural dependence on growth temperature is consistent with that derived from x-ray diffraction. Since in these samples Co films were deposited on amorphous carbon, it was not assumed that the epitaxial growth with substrate occurred.

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**Fig. 2.** Series of x-ray θ-2θ scans of 300-nm Co films with the scattering vector normal to the film plane as a function of the substrate temperature Ts.

**Fig. 3.** Electron diffraction pattern of 50-nm Co film deposited without heating.

**Fig. 4.** Electron diffraction pattern of 50-nm Co films deposited at 650 K.
It was found that polycrystalline hcp Co films grow on SiO₂ below 620 K and on amorphous carbon below about 650 K. Even though taking into account the error (± 20 K) in monitoring the substrate temperature we can say that these temperatures are slightly lower than the Tₘ (~690 K).

While hcp Co films deposited on unheated SiO₂ substrates had strong c-axis orientation of texture, as mentioned above, a different preferred orientation was observed for films grown on slideglass which were heat treated prior to deposition. Figure 5 shows x-ray θ-2θ scan of 30-nm Co film on such a slideglass. The substrate had been heated at 420 K for 3 h and cooled down to room temperature in the vacuum chamber, and then sputtering was took place without heating substrate. The diffraction pattern shows that the film has a orientation of (10.0) plane for hcp phase parallel to the film plane. The effect of this heat treatment on the crystallographic orientation was never observed on SiO₂. And, the same orientation with the case of SiO₂ substrates was observed, if slideglasses had not been heat treated.

Figure 6(a) and 6(b) show the hysteresis loops of (00.1) and (10.0) oriented hcp Co films, respectively. We can clearly see from these features that the (00.1) oriented film has large magnetic anisotropy perpendicular to the film plane, while in-plane anisotropy is dominant in (10.0) oriented film. This suggests that magnetocrystalline anisotropy of hcp Co crystallites occupies considerable part of the total anisotropy. Detailed analysis is in progress.

IV. SUMMARY

It has been demonstrated that hcp Co films can be produced on glassy substrates by GFS method. In the process the atoms deposited have very low kinetic energy; it must result in the formation of low temperature phase of cobalt. The crystallographic orientation of hcp Co films has been found to depend on the substrate. The reasons are not clear now.

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REFERENCES