Transactions of the Materials Research Society of Japan 30[4] 1027-1030 (2005)

The effect of oxygen partial pressure on the magnetoresistance of Co(-Pt)-ITO thin films

Wanti Ekawati[1], Ji Shi, Yoshio Nakamura, Osamu Nittono[2]
[1]Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology
Fax: 81-3-5734-3145, e-mail: wanti@mtl.titech.ac.jp
[2]Department of education, Material Science laboratory, Fukushima University
Fax: 81-24-548-3181, e-mail: onittono@educ.fukushima-u.ac.jp

We have proved that the microstructure and magnetoresistance of granular Co-ITO thin films can be controlled by thermal annealing. As it is known that the resistivity of ITO films is very sensitive to the partial pressure of oxygen during deposition, in this experiment we investigate the oxygen partial pressure dependence of magnetoresistance in Co(-Pt)-ITO thin films. The results show that the magnetoresistance increases with the increasing of oxygen partial pressure. However, excess oxygen partial pressure decreases the magnetoresistance of this film. On the other hand, the resistivity continuously increases with increasing of oxygen partial pressure, which is due to the oxidation of Co as shown by XPS analysis. The magnetoresistance of Co-Pt-ITO films show the similar tendency as Co-ITO film, but higher magnetoresistance value at optimum oxygen partial pressure. For Co-ITO, the magnetoresistance appears when the film consists of Co particles in crystalline ITO matrix. Film shows high resistivity due to the oxygen addition which strongly influence the resistivity of crystalline ITO. Meanwhile in the Co-Pt-ITO film, the magnetoresistance arises with amorphous ITO matrix. The existence of Pt is believed to stabilize the amorphous phase. Both Co-ITO and Co-Pt-ITO films show higher magnetoresistance at higher resistivity. The oxygen addition is proved to influence the film resistivity, structure and magnetoresistance of this film.

Key words: magnetoresistance, resistivity, oxygen, Co-ITO

1. INTRODUCTION

Recently, tunneling type magnetoresistance in granular material has been intensively reported in metal-insulator granular films. Several works on Co-Al-O[1], Co-Si-O[2], Fe-Al-O[3] show similar configuration where magnetic particles distributed in the insulating matrix. The resistivity of these films are relatively high in the order of 10^4-10^9 $\mu\Omega cm$[4]. In the previous work, we had observed the magnetoresistance in Co(-Pt)-ITO film where the resistivity and magnetoresistance could be controlled through thermal annealing[5]. As it is known that the resistivity of indium tin oxide (ITO) matrix is very sensitive to the oxygen addition during deposition, we investigate the oxygen partial pressure dependence on the magnetoresistance of Co-ITO and Co-Pt-ITO in this experiment. The oxygen influence on the resistivity, structure and magnetoresistance of Co(-Pt)-ITO films are explained at the present work.

2. EXPERIMENTAL PROCEDURE

Co-ITO and Co-Pt-ITO films are prepared using two-facing-target DC magnetron (TFTM) sputtering apparatus. The schematic diagram of two-facing-target magnetron sputtering apparatus is shown in Fig.1. Silica glass and Silicon wafer with the thickness of 0.5 mm were used as substrates for various characterizations. The sputtering chamber had been evacuated to a pressure around $8x10^{-5}$Pa before deposition. Argon and oxygen gasses were introduced into the sputtering chamber through mass flow controller. The mixed Ar + O_2 pressure was kept at 0.2 Pa during deposition. The oxygen partial pressure was controlled by changing the flow rate ratio of oxygen to argon gas. The film thicknesses were fixed around 2000 Å and the deposition rate was about 0.37 Å/sec. After the deposition, films were annealed in a vacuum for an hour at various temperatures. Structural properties of the films were characterized by X-ray diffraction. XPS measurement was used to identify the atomic composition ratio of each film. Film resistivity and magnetoresistance were measured using four-point probe MRHC-500 magnetoresistance measurement unit.

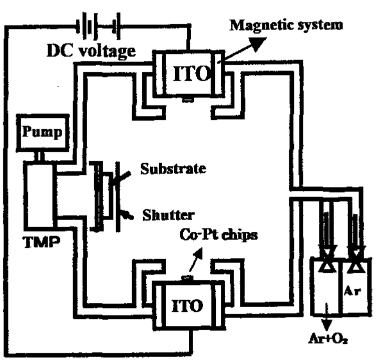

Fig.1. Schematic diagram of two facing target DC magnetron system.

The magnetic properties were examined using BHV-50H vibrating sample magnetometer (VSM). JEM3010 transmission electron microscope was used to observe the microstructure of the films.

3. RESULTS AND DISCUSSION

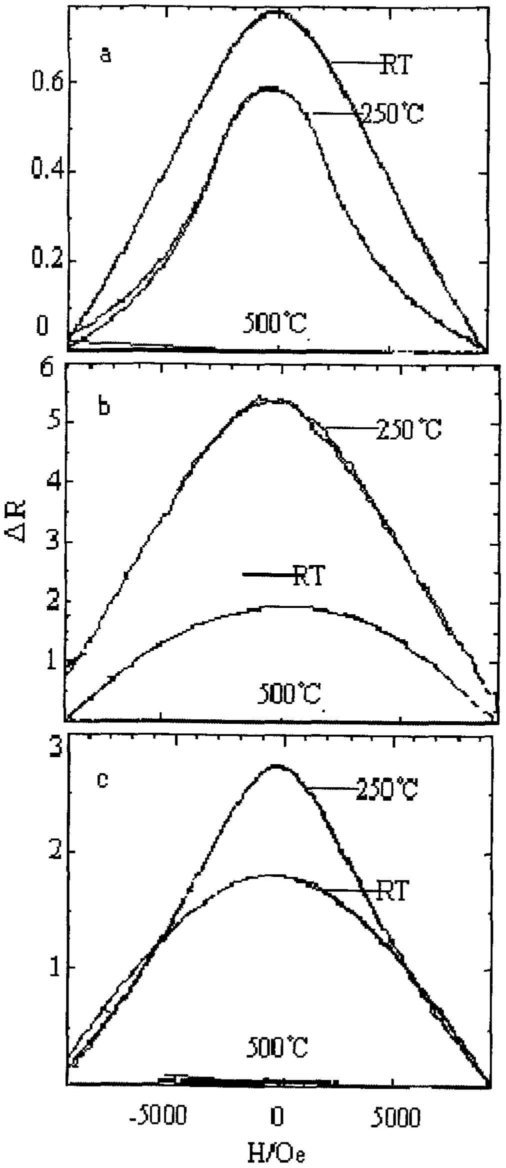

Fig.2. The ΔR(Ω) of Co-ITO films deposited at different oxygen pp and then annealed at various temperatures. a. without oxygen addition, b. 0.2% oxygen pp, c. 1% oxygen pp.

To understand the effect of oxygen partial pressure (pp) on magnetoresistance and their relation with thermal annealing, we observed the ΔR of Co-ITO films deposited at different oxygen pp and then annealed at various temperatures as shown in Fig.2. The volume fraction of Co to ITO is 1:2 in this experiment. Figure 2a shows the Co-ITO specimen annealed at different temperature without oxygen addition. In this figure, as-deposited film shows highest ΔR, and as increasing the annealing temperature ΔR continuously decreases. This is consistent with our previous research[5], considering the magnetic particle has already precipitated in the as-deposited film and through thermal annealing the magnetic particle size continuously increases, decreases the ΔR. However when oxygen is added in during deposition, film shows rapid increasing of ΔR values at 250℃ annealing temperature, ten times higher compared to specimen deposited without oxygen addition (Fig.2b). At higher oxygen partial pressure, the specimen show similar ΔR-T relation (Fig.3c).

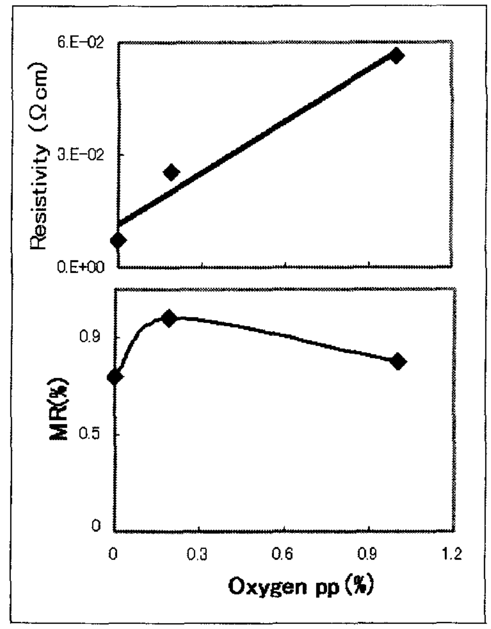

Fig.3. The magnetoresistance and resistivity of Co-ITO films as increasing of oxygen pp (T_a =250℃).

The resistivity and MR ratio of Co-ITO films as increasing of oxygen partial pressure are shown in Fig. 3. The MR ratio was measured at room temperature under the applied field of 10kOe. The specimen are annealed at 250 ℃ after deposition. Without oxygen addition introduced during deposition, specimen shows low magnetoresistance. As increasing the oxygen pp the magnetoresistance increases, however further increasing the oxygen pp the magnetoresistance decreases. On the other hand, the electrical resistivity continuously increases as increasing of oxygen partial pressure in this experiment.

As it is necessary to understand the magnetic properties of this film, we investigate the corresponding M-H curves of specimen deposited at different oxygen pp and then annealed at various temperatures. Figure 4a shows the M-H curves of specimen deposited without any oxygen, at room temperature film exhibits superparamagnetic behavior. Increasing of annealing temperature gradually increases the magnetization of this film and shows clear remanence at 350 ℃ annealing temperature. Further annealing at 500℃, the film shows clear hysterisis loop. When oxygen is added during deposition, specimen shows higher saturation magnetization as increasing the annealing temperature.

Further annealing at 500 ℃, film shows higher magnetization saturation and clear remanence appears.

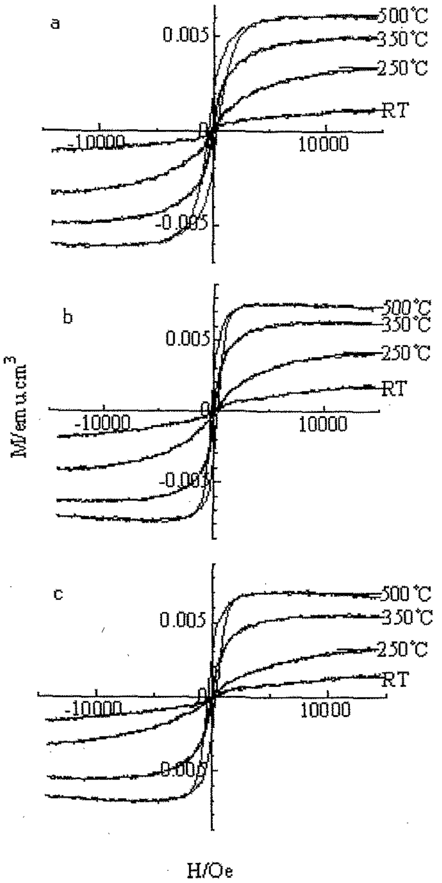

Fig.4. The corresponding M-H curves of Co-ITO films deposited at different oxygen pp then annealed at various temperatures. a. No oxygen, b. 0.19% oxygen pp, c. 1% oxygen pp.

Figure 4c shows the M-H curves of specimen deposited at 1% oxygen pp. This figure shows increasing of magnetization as increasing the annealing temperature. However at room temperature films has low magnetization, even thought after annealing at 250℃ film shows only small increases of magnetization. From M-H curves, we could notice that the further increasing of oxygen pp decrease the magnetic particles in as-deposited film. It is considered that the decreasing of magnetization is relevant to the increasing of resistivity due to oxidation of Co as shown in XPS analysis results (Fig.5).

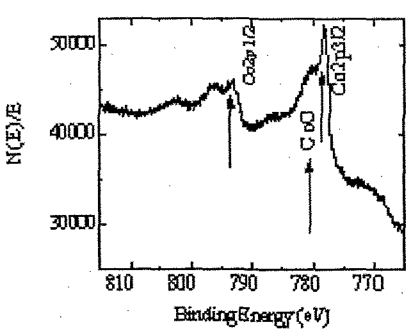

Fig.5. XPS result showing the oxidation of Co.

Clear information about the effect of oxygen on size distribution of magnetic particles and the structural properties of this film, however could not be seen clearly. For this reason, we investigate the microstructure of this film using transmission electron microscope (TEM) as shown in Fig.6.

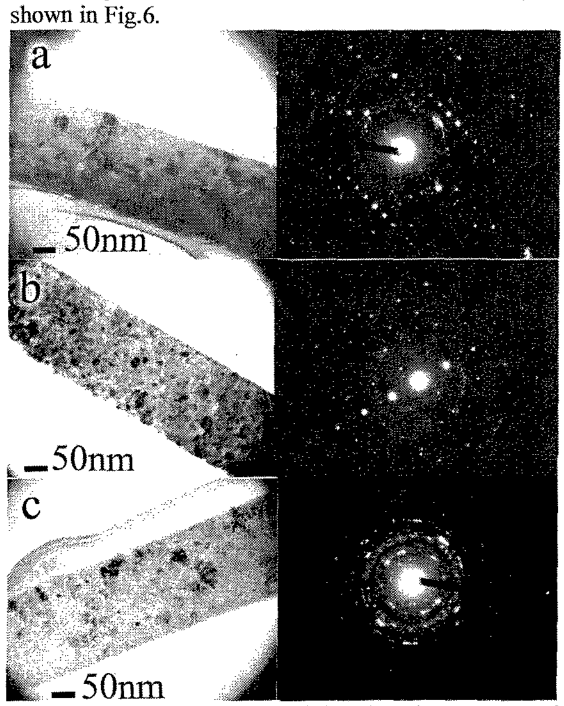

Fig.6. Bright field image and diffraction ring patterns of Co-ITO films deposited at different oxygen pp. a. no oxygen pp, b. 0.19% oxygen pp, c. excess of oxygen pp.

Figure 6a shows the bright-field images and diffraction pattern of Co-ITO films deposited without oxygen. This figure shows both the Co and ITO are in crystalline state. This film consists of large metallic Co grains in the size of 20nm. The distance between grains are narrow without almost no physical spacing. This explains the relative low resistivity and small MR found in this film. However, as increasing the oxygen pp film shows fine Co grains disperses in crystalline ITO matrix in the size of 5 to 15nm, which give rise to the magnetoresistance in this film. From the diffraction pattern as shown in Fig.6b, we could see that both of Co and ITO are in crystalline phases. The increasing resistivity in this film is due to the influence of oxygen pp on the ITO resistivity at crystalline phase. The increasing of oxygen is known to continuously increases the crystalline ITO resistivity. Figure 6c represents the microstructure of Co-ITO film when the excess of oxygen is found in this film. Both ITO and Co are in crystalline phases, however the ITO structure seems to growth in to bigger grain shape as shown in black grain of about 50nm in size .This film has very high resistivity in the order of $10^4 \mu\Omega cm$. The oxidation of Co particles is also considered to enhance the resistivity in this film.

The magnetoresistance that is found in Co-Pt-ITO films has similar tendency to Co-ITO films, only in higher MR ratio value which is observed at optimum oxygen partial pressure at 350℃ annealing temperature. Figure 7 represents the resistivity and MR ratio of Co-Pt-ITO films as increasing of oxygen pp during deposition. This films are annealed at 350℃ after deposition, where the optimum MR is observed in this film. The electrical resistivity of this film is continuously increases as increasing of oxygen pp. Without oxygen addition the specimen has low MR ratio. The increasing oxygen pp up to 0.19% pp increases the MR ratio, however further increasing oxygen decreases the MR ratio.

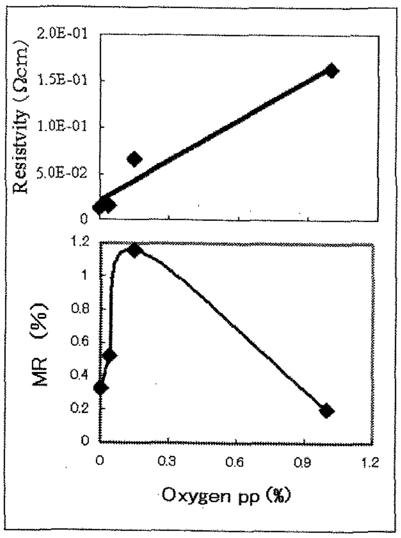

Fig.7.The MR ratio and resistivity of Co-Pt-ITO films as increasing the oxygen pp

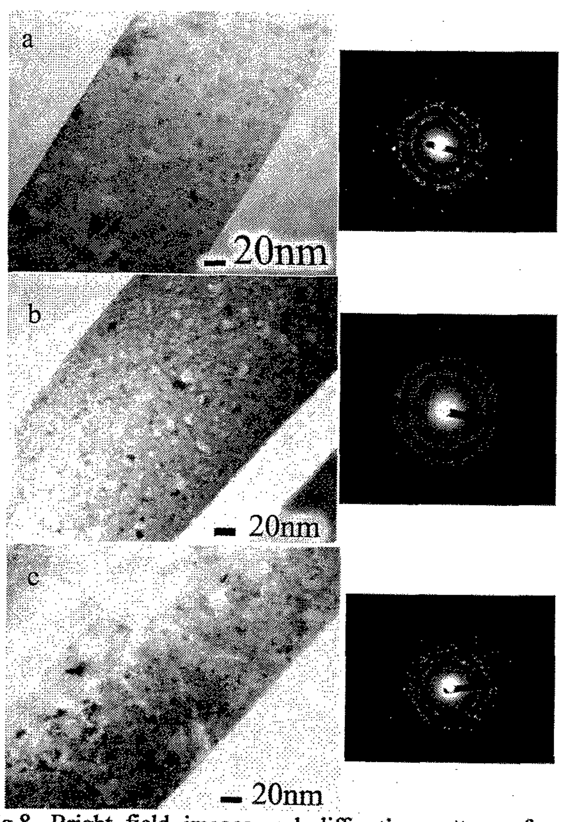

Fig.8. Bright field images and diffraction pattern of Co-Pt-ITO film as increasing of oxygen pp. a. no oxygen, b. 0.19% oxygen, c. excess of oxygen pp.

Figure 8 shows the microstructure of Co-Pt-ITO film as increasing of oxygen partial pressure. The phenomena of MR in this film is simply different compare to the magnetoresistance which is observed in Co-ITO films. Without addition of oxygen, we found fine Co are dispersed in amorphous ITO matrix but the some Co are growth in bigger shape, this probably could explain the relatively small MR in this film. However when oxygen is introduced during deposition, film consists uniform distribution of fine particle metallic Co dispersed homogeneously in amorphous ITO matrix with high resistivity. The average size of fine Co particles are around 5 to 10 nm. The certain additional of oxygen during deposition is found effective to enhance the MR ratio in this film. At higher addition of oxygen, specimen shows white long shape image which separate the magnetic particles. The addition of oxygen is considered to enhance the Indium oxide channel, which separate the grains, decreases the MR in this film. The addition of Pt is believed to stabilize the amorphous state in this film, keeping the ITO structure in amorphous phase.

4. CONCLUSION

The resistivity of ITO films is proved to be very sensitive to the partial pressure of oxygen during deposition. The magnetoresistance increases with the increasing of oxygen partial pressure. However, excess of oxygen decreases the magnetoresistance of such film. On the other hand, the resistivity continuously increases with increasing of oxygen partial pressure, due to the oxidation of Co as shown by XPS analysis. In Co-ITO case, the magnetoresistance appears when both Co and ITO are crystalline. Film shows high resistivity in this film due to the oxygen addition that strongly influence the resistivity in crystalline ITO. In Co-Pt-ITO film, the high magnetoresistance exists in amorphous ITO matrix. The resistivity of this film is relatively high in the order of 10^3-10^4μΩcm, compared to the other metal oxide. The existence of Pt is believed to stabilize the amorphous phase.

5. REFERENCES

[1]M.Ohnuma,K.Hono,H.Onodera,J.Appl.Phys.87,(2) 817 (1999)
[2]A.Milner. A.Gerber, B. Groisman, M.Karpovsky, A.Gladkikh, Physics. Rev. Letter 76,475 (1996)
[3]K.Kamei,M.Yonemura,K.Hanafusa, Journal of Mat. Science: Materials in electronic 12, 569-574 (2000)
[4]M.Ohnuma, K.Hono, E.Abe and H.Onodera, S.Mitani, H.Fujimori, J.Appl.Phys.82,(11)5646 (1997)
[5]Wanti Ekawati, Ji Shi, Yoshio Nakamura, Osamu Nittono, Trans. Magn. Research Soc.Japan 29[4] 1603(2004)

(Received December 24, 2004; Accepted February 28, 2005)