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Magnetoresistance of Co-Pt-ITO composites film

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Co-Pt-ITO thin films are prepared by two-facing-target DC magnetron sputtering, and then annealed at various temperatures to control the magnetoresistance. As-deposited film shows an amorphous phase with low resistivity. When the films are annealed at around 350℃, precipitation of Co-Pt metallic particles takes place in amorphous matrix, and leads to the highest magnetoresistance obtained in our experiments. Meanwhile, concentration of metal in the amorphous matrix decreases and film shows highest resistivity. The corresponding M-H curve shows slightly increase of saturation magnetization than those films deposited at room temperature. The existence of remanence is not detected and the film is still superparamagnetic. XRD patterns of films annealed at temperature higher than 400℃ exhibit crystalline ITO as well as the fcc CoPt. Resistivity of film decreased suddenly and magnetoresistance disappeared. Microstructure of films together with relation between resistivity and magnetoresistance are discussed from the viewpoints of size and distribution of magnetic phases.

Key words: Co-Pt-ITO, magnetoresistance, TFTM sputtering, resistivity

1. INTRODUCTION

In recent years, granular magnetic systems have been intensively studied due to their numerous technological application potentials. A granular magnetic system basically consists of nanometer-sized magnetic particles dispersed in a non-magnetic matrix[1]. Recently, the configuration of granular material has been widely reported both in metal-metal granular films such as Co-Cu[2], and in metal-insulator granular material as reported in Co-Al-O[3,4,5] and Fe-Al_2O_3[6]. In such metal-insulator granular systems, several methods have been applied in order to control the distribution of metallic magnetic particle. These methods include the controlling of Ar/O_2 partial pressure during sputtering[7], the adjustment of rotation speed of substrate holder during deposition[8] and particularly through thermal annealing[9]. The research reported in Co-Al-O granular film generally shows higher magnetoresistance at room temperature and after thermal annealing the magnetoresistance decreases[10]. In other words, the distribution of magnetic metal particle seems difficult to be controlled by thermal annealing.

In this work, we try to adjust the distribution of magnetic particles by controlling the precipitation of metallic magnetic particles from the amorphous matrix during thermal annealing. In view of the encouraging results obtained with Indium Tin Oxide (ITO) films in our previous work, we fabricated various films using amorphous ITO as matrix and Co-Pt as metallic magnetic particles. ITO is chosen as a matrix since it easily forms an amorphous phase and has lower crystallization temperature. Such Co-ITO and Co-Pt-ITO composites films are investigated in order to understand the annealing temperature dependence of magnetoresistance of this material, which is discussed in the viewpoints of size and distribution of magnetic phase.

2. EXPERIMENTAL PROCEDURE

Two-facing-target DC magnetron (TFTM) sputtering system was used in this experiment. In this sputtering system, ITO and Co-Pt targets were set parallel to each other as shown in Fig.1. Corning 7059 glass and SiO_2 glass 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. No oxygen was added, and Ar was the only gas that was introduced into the sputtering chamber. The Ar pressure was kept at 0.2 Pa during deposition. The sputtering voltage was kept at 500 volt and the sputtering current was fixed around 50 μA. Pre-sputtering was carried out for about 30 minutes with Ar gas before deposition to obtain an identical surface condition in each deposition. Film deposition itself was carried out for one and half hours. 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 using Cu Kα radiation. JEM3010 transmission electron microscope was used to take the high-resolution images. Film resistivity and magnetoresistance were measured using four-point probe MRHC-500 magnetoresistance measurement unit. The magnetic properties were examined using BHV-50H vibrating sample magnetometer (VSM).

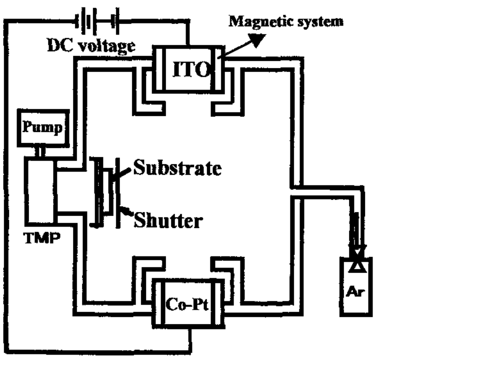

Fig.1. Schematic diagram of two facing target DC magnetron system.

3. RESULTS AND DISCUSSION

In this experiment, the result concerning Co-ITO film will be firstly described. Figure 2 represents the resistivity and magnetoresistance ratio of Co-ITO films annealed at various temperatures. As-deposited films have shown highest resistivity and MR ratio in this experiment, and with increasing the annealing temperature both resistivity and magnetoresistance gradually decreases. It is considered that metallic Co particles have already existed in the amorphous ITO matrix in as-deposited film. With increasing the temperature, the precipitations of metallic particles continue to occur, lowering the resistivity and MR ratio. Specimen annealed at 500°C exhibits the crystalline ITO and the magnetoresistance disappears. We are unable to control the distribution of metallic particles in this Co-ITO system, through thermal annealing.

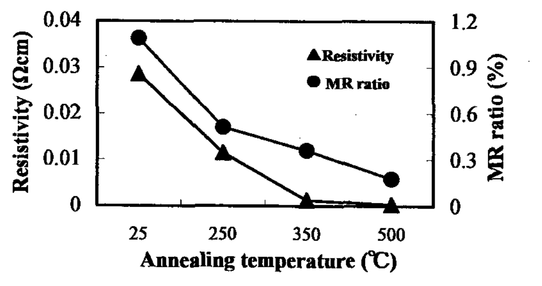

Fig.2. The resistivity and magnetoresistance ratio of Co-ITO films as a function of annealing temperature.

However, a drastic change of the thermal annealing effect is found in Co-ITO films with small addition of Pt as a second element. The atomic ratio of Co to Pt contained in Co-Pt-ITO film is around 5:1. The electrical properties of Co-Pt-ITO films annealed at various temperatures are shown in Fig.3. This figure reveals the relation between the resistivity and annealing temperature. As-deposited film has low resistivity compare to amorphous ITO. The specimen annealed below 300°C shows almost no change in resistivity. Upon further annealing up to 350°C, the resistivity increases rapidly and it reaches the maximum value at 370°C. Further annealing at above 400°C shows sudden decrease of resistivity.

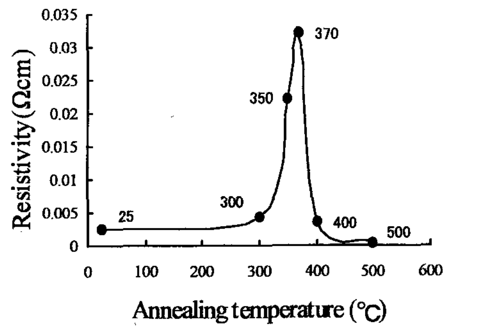

Fig.3. The resistivity of Co-Pt-ITO films as function of the increasing annealing temperature.

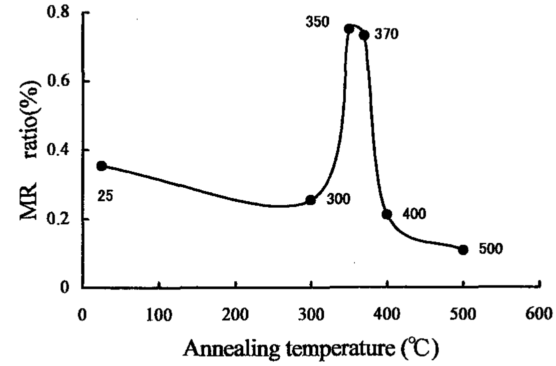

Fig.4. The MR ratio of Co-Pt-ITO films as function of annealing temperature.

The temperature dependence of magnetoresistance in Co-Pt-ITO film is also given in Fig.4. Magnetoresistance was measured under external magnetic field up to 10kOe, which was applied in plane of the films. All the measurements were carried out at room temperature. We define the magnetoresistance ratio as $\Delta\rho/\rho_{(0)}$x100%, where $\Delta\rho$ is equal to $\rho_{(0KOe)}-\rho_{(10KOe)}$. As-deposited film has small magnetoresistance ratio. With the increasing annealing temperature below 300°C, film shows slight decrease in magnetoresistance ratio. However, when the annealing temperature increases at above 300°C, film shows drastically increase of magnetoresistance and at 350°C film exhibits the maximum value. The specimen annealed at temperature above 400°C shows the decrease of magnetoresistance.

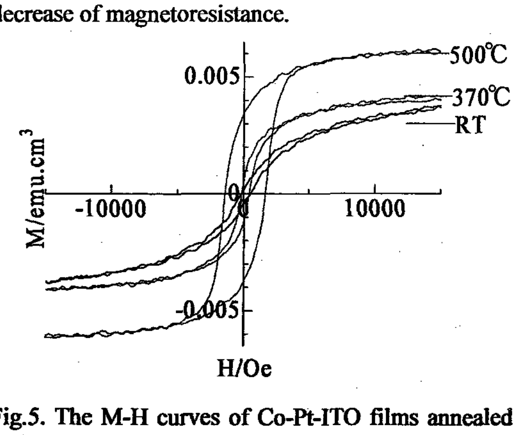

Fig.5. The M-H curves of Co-Pt-ITO films annealed at various temperature.

Figure 5 represents the M-H curves of Co-Pt-ITO films annealed at various temperatures. As-deposited film shows an amount of magnetization and superparamagnetic like behavior. The specimen annealed at 370°C shows slightly increase of the saturation magnetization with higher permeability but no existence of remanence is detected. The specimen annealed at 500°C has higher saturation magnetization and the remanence is observed.

To understand the structural properties of this film, we observed the X-ray diffraction pattern of specimen annealed at various temperatures, as shown in Fig. 6. As-deposited film shows an amorphous like pattern. The specimen annealed below 370°C has no crystalline peak, indicating the amorphous phase. Within further annealing at 500°C, film exhibits clear crystalline peaks of ITO and fcc Co-Pt. However, the XRD pattern of specimens annealed at 400°C presents the broaden peaks, which could not clearly identified. The occurrence of metallic particles could not be clearly detected in X-ray diffraction pattern of the specimen annealed below 370°C, therefore for more precise analysis the electron diffraction observation is needed.

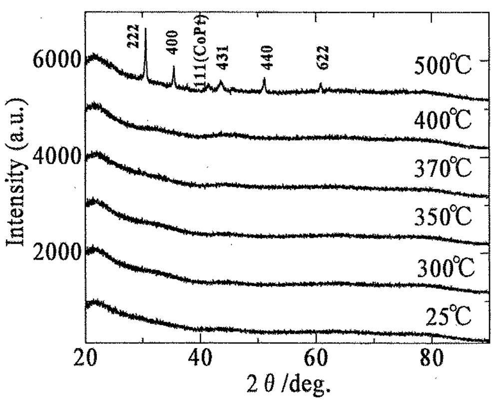

Fig.6. XRD pattern of Co-Pt-ITO films annealed at various temperature.

In order to get the information concerning the size and distribution of metal precipitation in matrix, the microstructures of specimen annealed at various temperatures are observed by TEM. The results are given in Fig.7. As-deposited films basically consist of amorphous phase as shown in Fig. 7a. This film has lower resistivity than pure amorphous ITO because the specimen contains large amount of metal elements in the matrix. The specimen annealed at 350°C has amorphous matrix and metallic particles with the size around 8 nm as seen in Fig. 7b. We could confirm that the metallic particles are in crystalline phases by HRTEM. The microstructure of Co-Pt-ITO film annealed at 500°C shows the metallic particle that has grown up to 20 nm in size. In this figure, the ITO matrix and fcc Co-Pt are both in crystalline phases. Corresponding to the TEM micrographs we also observed the diffraction patterns. The diffraction of as-deposited film shows a halo pattern, representing the amorphous phase. Specimen annealed at 350°C shows a halo pattern and weak metal rings of fcc Co-Pt particles, which are identified as 111 and 220. Upon further annealing at 500°C, specimen shows clear ring patterns of crystalline ITO.

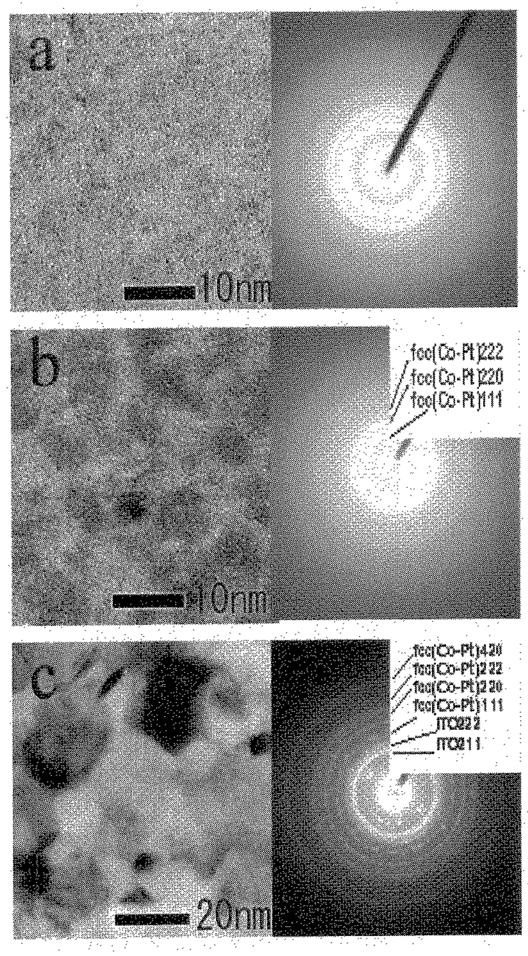

Fig.7. TEM micrograph and diffraction ring patterns of Co-Pt-ITO films. a. at RT, annealed at b. 350°C and c. 500°C.

Based on the above experimental results, we could summarize the structural, electrical and magnetic properties. As-deposited films are basically amorphous and the resistivity is lower than the pure amorphous ITO. This film show superparamagnetic behavior and magnetoresistance. Although the film is amorphous, it is considered that there exist magnetic clusters in the amorphous matrix that lead to small magnetoresistance. Film annealed at 350°C still has an amorphous matrix with crystalline Co-Pt magnetic particles. Resistivity of this film increases because concentration of the matrix decreases. Metallic particles with size of nanometer distribute in the matrix lead to the highest MR in our experiments. When films are annealed at 500°C, crystallization of ITO starts so that resistivity of the film suddenly decreases and magnetoresistance disappears. This film has the remanence with higher saturation magnetization. It is noted that the highest MR and highest resistivity are achieved at the same time. If the crystallization of ITO matrix with certain amount of metallic element does not start at around 400°C, we probably could get higher MR film. It means that the control of the crystallization temperature of amorphous ITO is important to our study.

4. CONCLUSION

As-deposited film containing small amount of Pt in Co-ITO films is basically amorphous with low resistivity. At around 350°C to 370°C, the precipitation of crystalline Co-Pt particles occurs in the amorphous matrix, decreasing the metal concentration which leading to highest resistivity. In the meantime, the distribution of metallic particles with the size of nanometer in ITO matrix leads to maximum MR. Upon further annealing at above 400°C, the crystallization of ITO matrix started, as the result the film resistivity decreased and magnetoresistance disappeared. The structure of fine Co-Pt particles distributed in amorphous ITO matrix can be successfully controlled through thermal annealing and achieve the magnetoresistance, this film shows highest magnetoresistance at highest resistivity.

5. REFERENCES

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