Magnetoresistance effect, Magnetism, and Microstructure in Co-Au Granular Alloy Films Produced By Pulsed Electrochemical deposition

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This paper discusses the relationship among the magneto-resistance (MR), magnetic properties, and microstructure of the Co-Au granular alloy prepared by pulsed electrochemical deposition. It is shown that MR ratio of the Co-Au single layer (100 nm) film deposited at the current density of 5 mA/cm^2 increases with increasing Co concentration in the film and reaches a maximum of 4.4% at 40at%Co. It is observed that both the MR ratio and grain sizes in the films are dependent on the current density values.

Keywords: pulse electrodeposition, magnetic properties, magnetoresistance effect, microstructure, Co-Au granular films

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1. Introduction

Since the discovery of giant magnetoresistance (GMR) in the metallic Fe/Cr multilayer film [1] the studies on the physical properties of many other nano-ordered multilayer films have not only attracted attention in the fundamental physics but also in electronic engineering [2-4]. The GMR effect has also been observed in many granular alloy system composed of ferromagnetic and non-ferromagnetic metals. [5-11]. The response of the magnetic field and GMR strongly depends on the Co at % of the layers; however, it is not yet clear how the size of the GMR is related to the microstructure of the film. On the other hand, GMR is very sensitive to some preparation parameters, such as composition, layer thickness, inter-granular roughness, grain size etc. [5]. It is believed that the mechanism responsible for GMR is based on spin-dependent electron scattering within magnetic particles, and at the interface between ferromagnetic and non-magnetic components.

Most of the research on giant magnetoresistance (GMR) effect in multilayer films is based on films grown mainly from non-aqueous phase [3,12]. Although pulse electrochemical deposition is not a simple method for deposition, it enables one to grow alloy and metallic multilayers of generally immiscible metal combinations by controlling the electrochemical parameters [7-13]. By reducing the pulse size of the deposition for the multilayers to a very small value, a multilayer film with layers of two different atomic compositions eventually results in a binary alloy of a solid solution-type mixed in the atomic level.

This paper discusses the preparation of the binary alloy films of Co-Au in a specially developed cyanide solution at a constant current density by means of a computer-controlled pulse electrodeposition. Magnetic, magneto-transport, X-ray diffraction, and low-temperature magnetization measurements are used to obtain information about the mechanism underlying GMR. A relationship among magnetic, magnetotransport properties, and microstructure of the Co-Au alloy films is examined as the concentration of Co is varied.

2. Experimental

The samples were prepared in an electrochemical cell using a computer controlled pulse electrochemical method. The electrolyte for the deposition of alloy was composed of $CoSO_4.7H_2O$, $KAu(CN)_2$, $Na_3C_6H_5O_7.2H_2O$, and NaCl. The bath constituents are similar to Ref [13] with one important consideration that the cyanide species have been added. The composition of Co in the electrolyte is changed while keeping the concentration of Au constant. This way the ratio between the Co and Au is varied. The composition of the bath was varied from 10 to 98 at% of Co, while keeping the Au, Na-citrate, and NaCl constant. The purpose of adding sodium chloride was to enhance the conductivity of the electrolyte. The use of Na-citrate was to improve processing conditions and material properties. Pulse current plating was used for Co-Au alloy plating. Different current densities, ranging from 0.1 mA/cm^2 to 20 mA/cm^2 were tested to deposit pure Au and Co-rich alloys. In pulse plating, the layer thickness can be kept constant by controlling the plating time. Co-Au granular alloy film was fabricated using galvanostatic square-wave pulsed plating with currents ranging from 0.1 mA/cm^2 to and 20 mA/cm^2 with variable times (0.01~10 sec). The nature of the substrate, upon which the plating occurs, has substantial influence on electrodeposits, their structure and properties. This is particularly true when the deposit is in the nano-order scale. The substrates were 15 nm Cu (111) thin films vapor deposited on the glass plate. The chemical cleaning with 1 M H_2SO_4 solution was performed to remove the oxide film on the copper disk surface. The energy-dispersive X-ray analysis (EDAX) analytical method was used to measure the composition and thickness of the deposited alloy films.

Electrical resistivity was measured using the standard four-point probe ac technique with an excitation current of 3 mA. The MR measurement was made in the plane of the films under the magnetic field range of 0 to 21 kOe both perpendicular and parallel with respect to the current. The four point contacts were mechanically aligned with an accurate precision that permitted us to arrange the current path parallel or perpendicular to the applied magnetic field by rotating the sample holder. MR ratio was defined as MR%= [R(H)-R(H=0)]x 100% /R(H=0). Magnetization was measured using a Vibrating Sample Magnetometer (VSM) with applied field of 1 kOe to study the particle size effect on the magnetization and magnetoresistance effect. The structural characteristics of the as-

deposited and annealed samples were investigated using Rigaku Cu-kα diffractometer and Braggs law: $n\lambda = 2d \sin\theta$. The temperature dependence of zero-field-cooled (ZFC) and field-cooled (FC) magnetization in the as-deposited and annealed state is studied using rf-Squid meter. The mean Co particle size was estimated using the relation $K_A v = 25\ k_B T_B$, where K_A is the magnetic anisotropy energy density constant for the fcc-Co, v is the volume of the super paramagnetic Co particle corresponding to the blocking temperature T_B, and k_B is the *Boltzman* constant.

3. Results and Discussions

3.1 Compositional Analysis

Fig. 1 shows the correlation of Co concentration in the electrolyte and the thin films deposited at the current densities of 1, 3, and 5 mA/cm^2, respectively. The composition relationship is not a linear. It is observed that an atom of less noble element, i.e. Co, is less readily deposited in the films. Therefore, it is concluded that the system is of regular alloy type. Co concentration of the deposited films is lower in the lesser concentration region of the bath.

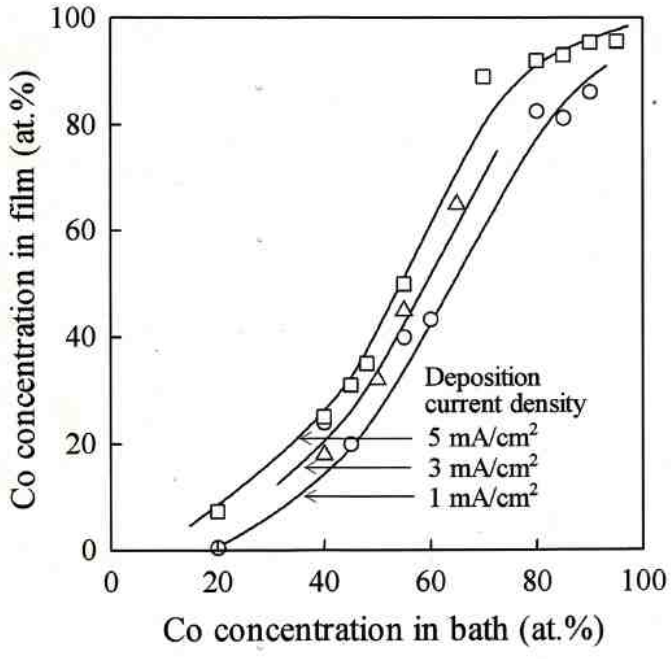

Fig. 1 Co concentration in the single electrolyte and the corresponding film composition of Co in the Co-Au single layer film for the current densities of 1 (denoted by open circles: o), 3 (denoted by open triangles: Δ) and 5 mA/cm^2 (denoted by open squares), respectively.

However, the concentration in the film increases abruptly for a bath composition in excess of 50 at% of Co. The composition of Co in the film tries to reach the composition of film at higher current density i.e. at current density of 5 mA/cm^2 in our experiment. Also, the concentration of the Au atoms is very small as compared to the concentration of Au in the film. Therefore, the deposition of Au atoms seems to be under the diffusion control.

3.2 Composition dependence of magnetoresistance ratio

Fig. 2 shows the Co concentration dependence of the MR ratio for the Co-Au single layer deposited at current densities of 1, 3, and, 5 mA/ cm^2, measured at room temperature and within the magnetic field of 21 kOe. The maximum MR ratio of the films deposited at 1 mA/ cm^2 is 2.0%. Increasing the current density to 5 mA/cm^2, the MR ratio increases largely for all Co concentration of the film. The maximum shows the value of 4.4 % and the concentration of the maximum shifts slightly towards the lower Co concentration. It is observed that the maximum of the MR ratio appears at a narrow concentration range of ferromagnetic atoms even if they are deposited at different current densities.

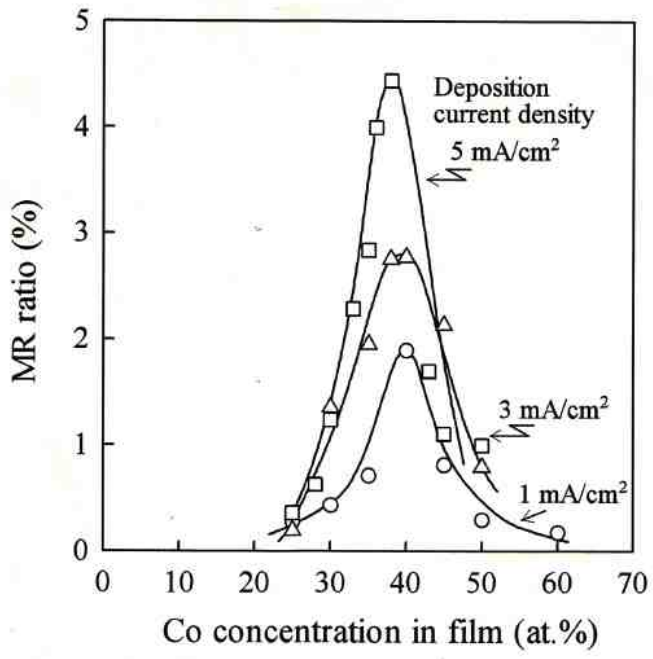

Fig. 2 Concentration of Co in the film as a function of the MR ratio for the Co-Au single layer films deposited at the current densities of 1(denoted by open circles: o), 3 (denoted by open triangles: Δ), 5 mA/cm^2 (denoted by open squares), respectively.

The increase of MR ratio near the 30at % Co is seems to be due to the optimum size and distribution of Co granule and inter-granular separation. The low values of MR for the film below 30at% Co can be ascribed to a relatively low concentration of ferromagnetic components leading to fewer magnetic and non-magnetic interfacial scattering sites. The decrease in MR ratio above 45 at % Co and higher seems to be due to the decrease in spin dependent scattering, which is mainly responsible for the GMR effect. It seems that the increase in the MR ratio of the film with an increase in the deposition current density is owing to a change in microstructure of the film.

3.3 Composition dependence of the saturation magnetization

Fig 3 illustrates the composition dependence of the saturation magnetization (emu/gm) in the Co-Au alloy. The magnetization deviates from the simple dilution law, and decreases with decrease in the concentration, and vanishes at the 30 at % Co. The tendency of the decrease is more abrupt for the current density of 5mA/cm^2 in comparison with the current density of 1 mA/cm^2.

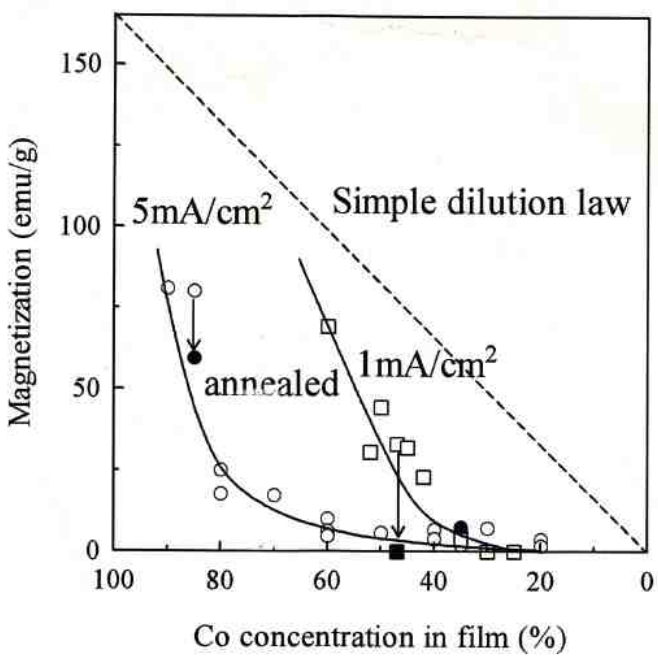

Fig. 3 Composition of Co in the alloy as a function of the saturation magnetization. Both the dark circles and squares represent magnetization due to annealing. The dotted line represents the simple dilution law.

The decrease in the magnetization suggests that the Co-Au alloys electrodeposited at the higher current density formed small grain sizes or solid solution of the Co and Au atoms. After annealing the films at 573 K for 1 hour, the magnetization further decreases.

3.3 Microstructure Analysis: X-ray diffraction patterns

Fig. 4 shows X-ray diffraction patterns of the as-deposited $Co_{35}Au_{65}$ films deposited at the current densities of 1, 3 and 5mA/cm^2, respectively. The precipitation of the fine Co and Au particles is estimated from the X-ray pattern. The patterns demonstrate that films have fcc structure with a weak fcc-Co. The hcp peak of Co is not visible. The Au (111) diffraction peak position appears almost in the same diffraction angel (2θ) position irrespective of the value of the current densities. As the ferromagnetic layer of the films contain a considerable percent of Au atom, the appearance of strong fcc-Au <111> is not unlikely. However, the Au (200) or fcc-Co (111) line is broader for the films deposited at the higher current density.

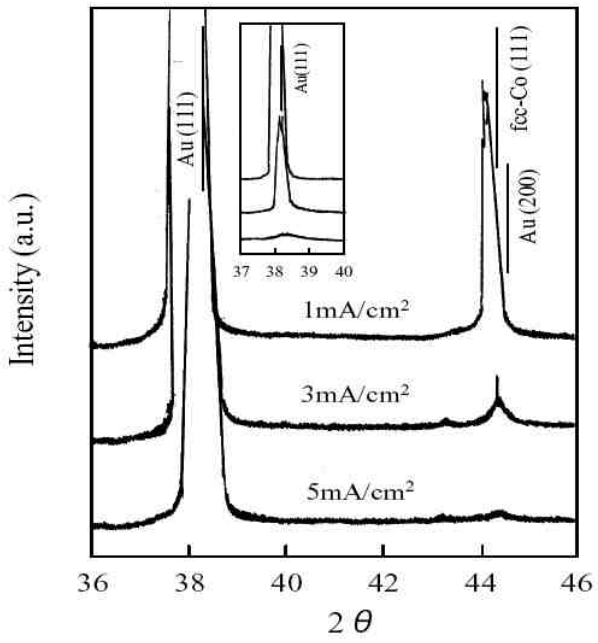

Fig. 4 Diffraction patterns for the as-deposited $Co_{35}Au_{65}$ alloy films at the current densities of 1, 3 and 5 mA/cm^2. The inset suggests that the Au (111) peak line is the strongest in all current densities.

It could also be considered that smaller Co particles or grains have been precipitated in the films deposited at higher current densities. The inset shown in the upper side also

suggests that the Au (111) peak line is the strongest in all cases, indicating preferential orientation of the crystallites along [111] direction in all the samples.

3.4 Estimation of Co particle size

Fig. 5 shows the temperature dependence of zero-field-cooling (ZFC) and field-cooled (FC) magnetization for the Co-Au alloy films in the as-deposited and annealed (573K for 1hour) states . The samples were first cooled to 5 K at 50 Oe. However, the magnetic moment is measured during the heating cycle in the range of 5K ~ 300K. This measurement is found to be extremely sensitive to particle interactions [15] and provide a good technique for investigating the energy barrier distribution. In the as-deposited sample, a broad peak is observed near the temperature of 65K and 45K at the deposited current densities of 3 and 5 mA/cm^2, respectively. If the peak temperature is the mean blocking temperature observed for super paramagnetic behavior, the existence of the peak at the lower temperature side suggests that the very fine particles of the ferromagnetic Co or Co-Au alloy phase may have been precipitated in the alloy film and they have a wide distribution in their size [16].

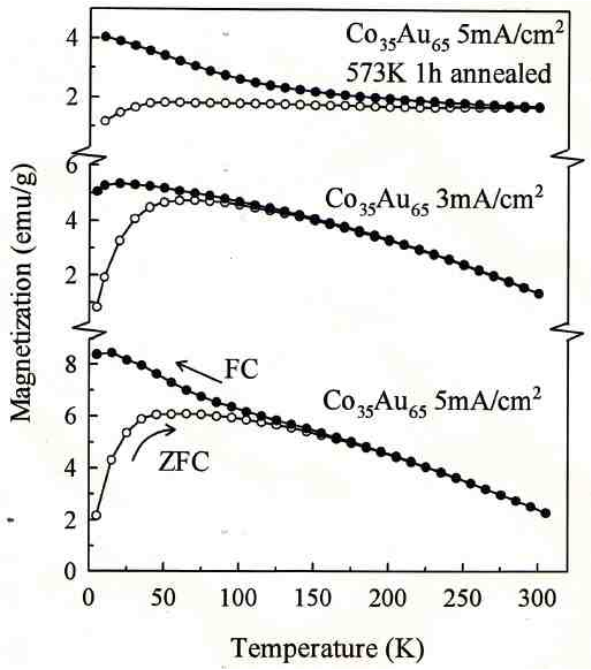

Fig. 5 Temperature dependence of zero-field-cooling (ZFC) and field-cooled (FC) magnetization for the Co_{35}-Au_{65} alloy films at a field of 50 Oe in the as-deposited state and after annealing at 573K for 1hour

The mean Co particle size is estimated using the relation, $K_A v = 25\ k_B T_B$, where K_A is the magnetic anisotropy energy density constant for the fcc-Co, v is the volume of the super paramagnetic Co particle corresponding to the blocking temperature T_B, and k_B is the *Boltzman* constant. Since the Co-rich magnetic particles are present in the matrix as fcc phase, taking K_A equal to 5.5×10^{17} eV/cm^3 (1 eV = 1.6×10^{-19} C) corresponding to the bulk fcc Co, the volume of the particle is calculated. Assuming the spherical shape for the particles, the estimated mean Co particle diameter corresponding to the blocking temperature is estimated as an approximately 40Å. Co particle sizes deposited at a current density of 5 mA/cm^2 (corresponding to the blocking temperature of 45K) are slightly smaller than those of 3 mA/cm^2 (corresponding to the blocking temperature of 65 K). The peak in the ZFC curve of the annealed sample was not observed at a temperature lower than 300K. It is apparent that the clusters in these annealed films have a range of blocking temperatures, which extend at least to room temperature suggesting the increase in the size and interaction effects of magnetic particles with a wide distribution. For the as deposited films, it is possible that the small Co particles present in Co-Au films deposited at 5mA/cm^2 contribute to the larger MR values for these films.

4. Conclusions

Co-Au granular alloy films have been prepared by using a computer-controlled pulse electrodepositing method. X-ray diffraction for the Co-Au alloy system revealed that the film has smaller particles at higher current density. The MR ratio for the single layer Co-Au alloy system deposited at the current density of 5 mA/cm^2 shows a maximum of 4.4% at 40 at % of Co. The MR ratio and grain size in the film largely depended on the change of current densities. The temperature dependence of the magnetization at low temperature suggests the formation of fine particles showing super-paramagnetic behavior. The presences of small Co particles in the Co-Au films deposited at 5 mA/cm^2 contribute to the larger MR values for these films. This work is significant because of its usefulness for devices and application in thin film industries.

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