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Fabrication and magnetic properties of highly ordered $Co_{16}Ag_{84}$ alloy nanowire array

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Abstract. Highly ordered Co−Ag alloy nanowire arrays embedded in the nanochannels of anodic alumina membranes (AAMs) were successfully fabricated using electrodeposition. Scanning electron microscopy and transmission electron microscopy observations revealed that the ordered Co−Ag alloy nanowires were uniformly assembled into the hexagonally ordered nanochannels of the AAMs. Magnetic measurements showed that the perpendicular coercivity ($H_c \perp$) of the ordered nanowire arrays increased dramatically as the annealing temperature (T_a) rose from 300 °C, reached its maximum (183 Oe) at 400 °C and then decreased sharply as T_a further increased beyond 400 °C. However, there was little change in the parallel coercivity ($H_c \parallel$) of the nanowire arrays during the annealing process. The mechanism of this phenomenon was attributed to the special structure of the AAMs and nanowires.

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In recent years, one of the most interesting and intensely investigated classes of materials has been that of magnetic films and nanowires, due to not only the fundamental interest in these materials but also the potential applications of some of their properties [1, 2]. In particular, the fabrication of ordered magnetic metal nanowire arrays has attracted considerable scientific and commercial attention due to their potential utilization in magnetic recording [3, 4]. For example, nanoscale patterned arrays have been suggested as suitable recording media for achieving recording densities of more than 100 Gbit/in^2 each memory unit being stored in a single array [5, 6]. This storage density is much higher than that of current commercial hard disks (3.7 Gbit/in^2), and is also beyond the projected thermal limit of 40 Gbit/in^2 for continuous magnetic films [7]. Very recently, Blythe et al. have fabricated Co−Cu magnetic alloy nanowires into track-etched polymer membranes by electrodeposition, and have presented a preliminary study of their magnetic properties [8]. In this work, we used anodic aluminum membranes (AAMs) as templates to fabricate the ferromagnetic-nonmagnetic alloy nanowire arrays using electrodeposition. AAMs have two significant advantages over the track-etched polymer membranes used in the fabrication of ordered nanostructures. Firstly, it is well known that AAMs grown in acid electrolytes possess hexagonally ordered porous structures with high nanochannel density in the range 10^9–10^{11} mm^{-2} [9]. Secondly, AAMs are stable at high temperature [10], which opens up the possibility of studying how annealing modifies the magnetic properties of alloy nanowires. Here we report the use of electrodeposition to fabricate ordered Co−Ag alloy nanowire arrays in the nanochannels of AAMs, and the annealing temperature dependence of their magnetic properties has been studied.

1 Experimental procedure

1.1 Anodic alumina membranes (AAMs)

Through-hole AAMs, with pore diameters of about 60 nm and thickness of about 50 μm, were prepared using a two-step anodization process [11] to oxidize aluminum in acid solutions. The aluminum plates (99.999% purity, 0.3 mm thickness) were degreased in acetone, and then annealed in a vacuum of about 10^{-5} Pa at 400 °C for 4 h to remove mechanical stress and to induce re-crystallization. The aluminum plate was then electropolished under a constant current condition of 90 mA/cm^2 for 3 min in a mixture of $HClO_4$ and C_2H_2OH at room temperature to smooth the surface morphology. The aluminum plate was anodized in 0.3 M oxalic acid ($C_2H_2O_4$) electrolyte. The anodizing voltage was 40 V and the temperature of the electrolyte was kept constant at 17 °C. After 3 h anodization, the plates were immersed in a mixture of 6 wt % H_3PO_4 and 1.8 wt % H_2CrO_4 at 60 °C for 7 h to remove the alumina layers. Then, the aluminum plate was anodized again for 6 h under the same conditions as the first step. At the bottom of the AAM, the aluminum layers present were removed using saturated $HgCl_2$ solution. A subsequent etching treatment was carried out in 6 wt % H_3PO_4 at 30 °C for 70 min to remove the barrier layer on the bottom of the AAM.

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1.2 Electrodeposition and annealing

A gold film was sputter-deposited on one side of the membrane, to serve as the working electrode in a two-electrode electrochemical cell. The electrolyte contained 40 g/L $CoSO_4 \cdot 7H_2O$, 50 g/L $AgNO_3$, 60 g/L NH_3H_2O and 40 g/L CH_3COONH_4. The electrodeposition was carried out at a constant current density (1.5 mA/cm^2), with carbonate serving as the counter electrode at room temperature for 6 h.

After electrodeposition, the ordered $Co_{16}Ag_{84}$ alloy nanowire arrays embedded in the AAMs were annealed at different temperatures T_a (300, 400, 500 and 600 °C) for 1 h in a furnace under a flowing Ar atmosphere. The magnetic properties were measured using vibrating sample magnetometry (Lakeshore, VSM-5s-15), with the applied field either parallel or perpendicular to the surface of the samples. The coercivity (H_c) and the saturation magnetization (M_s) were obtained from the hysteresis loops.

For observation using the scanning electron microscope [(SEM) JEOL JSM-6300], small pieces of AAM with a sample of the ordered Co−Ag alloy nanowire arrays were eroded by an aqueous solution of 5 wt % NaOH in order to remove either the upper part of the AAM or the whole AAM. They were then washed with distilled water several times and dried in air.

The morphology of these alloy nanowires was obtained by transmission electron microscope [(TEM) JEM-200CX] after having completely dissolved the AAM in an aqueous solution of 5 wt % NaOH. Some of the alloy nanowires remained in the solution. A drop of the solution was placed on a Cu grid with a carbon film and allowed to dry prior to electron microscope analysis.

The chemical compositions of these alloy nanowire arrays were determined by energy-dispersed X-ray spectrometry (EDS) and their phase structural characterizations were carried out by X-ray diffraction [(XRD) MXP18AHF] by means of an automated diffractometer using Cu K_α radiation.

2 Results and discussion

2.1 Characterization

The typical top view and cross-section SEM images of Co−Ag nanowire arrays (Fig. 1a and b, respectively) demonstrate that the deposited alloy, does indeed fill the nanochannels uniformly and that the nanowires are apparently continuous and parallel. It is estimated that the density of the alloy nanowires is about 10^9–10^{11} mm^{-2}, which is beneficial for enhanced magnetic recording. A representative TEM image of a $Co_{16}Ag_{84}$ alloy nanowire extracted from an AAM is shown in Fig. 1c. It can be seen that the $Co_{16}Ag_{84}$ alloy nanowire is uninterrupted with a diameter of about 60 nm, which corresponds to the diameter of the nanochannel of the AAM used. Energy-dispersed X-ray spectrometer (EDS) analysis during SEM observation process (Fig. 2) suggests that the relative atomic concentrations of Co and Ag in the nanowires is close to the nominal stoichiometry ratio 16:84 .

We know that, under equilibrium conditions, the mutual solubility of Ag and Co is very low in both the solid and liquid forms. However, under non-equilibrium conditions, the Co/Ag system could form a metastable solid solution. In this type of material, the annealing treatment results in the recrystallization of the metastable Co−Ag alloy into separate Co and Ag phases, leading to the formation of small Co particles which exhibit greatly enhanced magnetic properties because of their single-domain nature [15]. This process has already been proved by XRD. In Fig. 3, it can be seen that the as-deposited sample is single-phase fcc Ag, but the Ag diffraction lines are shifted toward higher angles. Therefore the as-deposited alloy nanowires in this work are a solid solution.

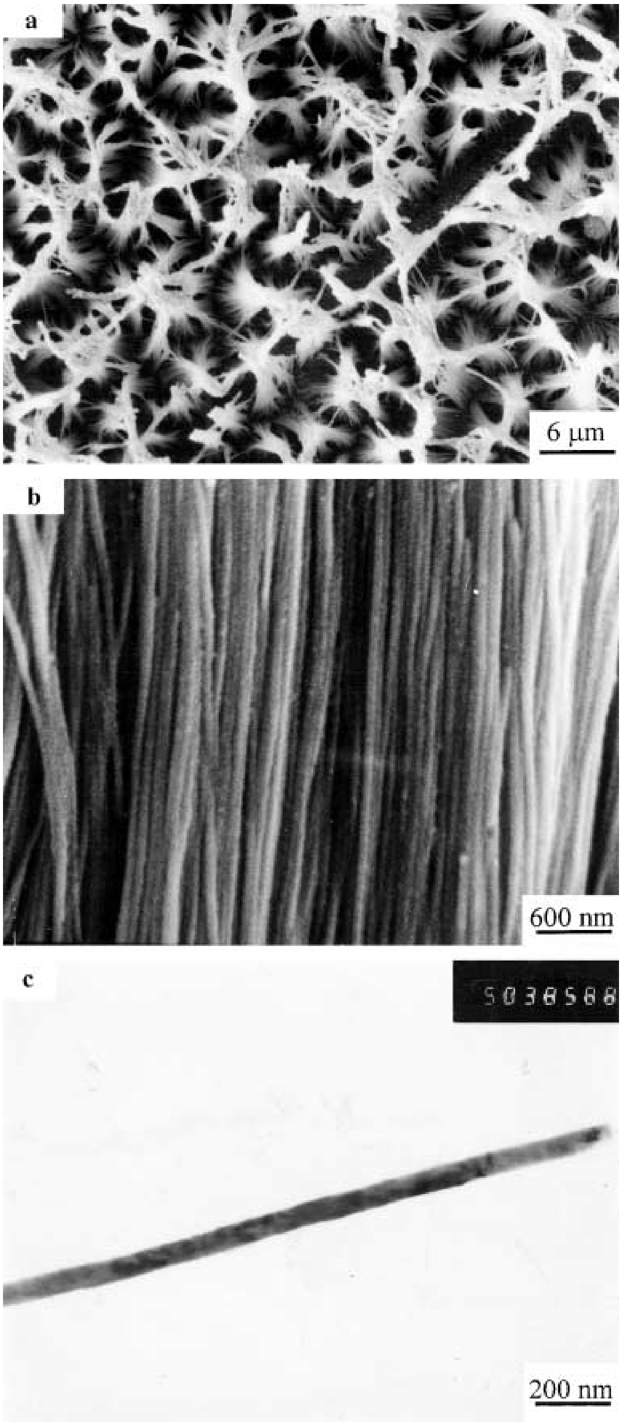

Fig. 1a–c. SEM images of a $Co_{16}Ag_{84}$ alloy nanowire array (**a** and **b**), and representative TEM image of a $Co_{16}Ag_{84}$ nanowire extracted from the AAM (**c**)

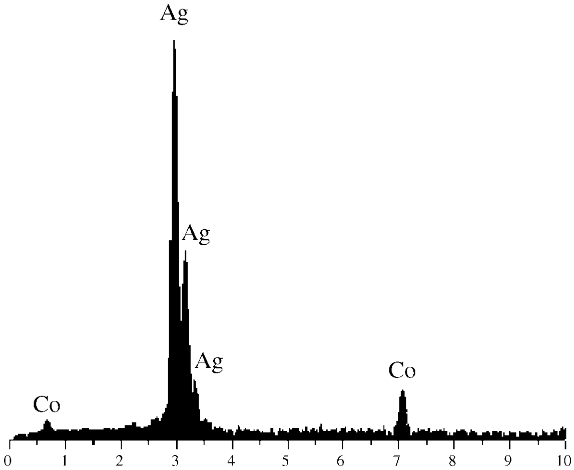

Fig. 2. The energy-dispersed X-ray analysis spectrum of the $Co_{16}Ag_{84}$ alloy nanowires in Fig. 1a

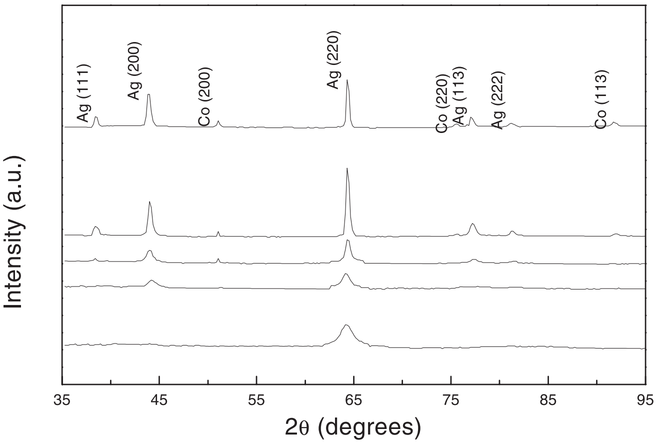

Fig. 3. X-ray diffraction spectra of $Co_{16}Ag_{84}$ alloy nanowire arrays at room temperature, after annealing for 1 h at various temperatures T_a

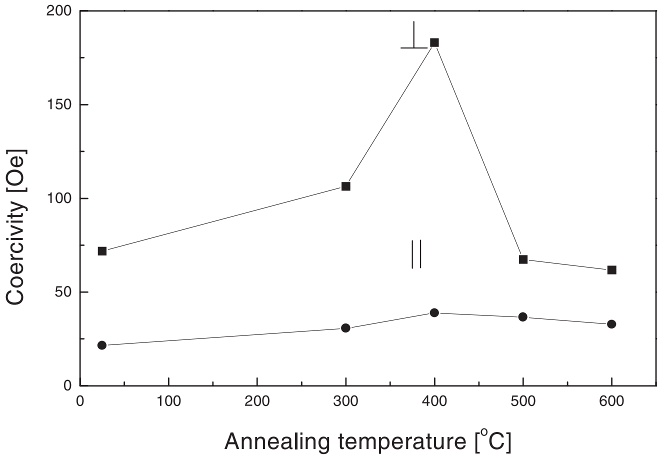

Fig. 4. Room-temperature coercivity of $Co_{16}Ag_{84}$ as a function of annealing temperature T_a, measured with the external field applied parallel (∥, *circles*) and perpendicular (⊥, *squares*) to the plane of the sample

The fcc structure is preserved up to $T_a = 300\,°C$. After further annealing at 400 °C, however, the fcc Co lines appear, indicating the recrystallization of the metastable Co−Ag alloy into fcc Co and fcc Ag. As T_a is increased over 400 °C, the diffraction lines become progressively narrower due to the growth of particle size.

2.2 Magnetic properties

2.2.1 Coercivity. The effect of annealing temperature (T_a) on the coercivity measured at room temperature is shown in Fig. 4 for the ordered $Co_{16}Ag_{84}$ alloy nanowire arrays. At first, we note that the coercivity measured with the external field applied perpendicular to the sample surface ($H_c \perp$) is always larger than that of the parallel one ($H_c \parallel$), due to the preferential orientation of the nanowires [12].

The evolution of $H_c \perp$ with increasing annealing temperature is found to be the same as for Co−Ag, Fe−Ag and Co−Cu alloy films [12–14]. While X-ray diffraction analysis indicates that only a singe phase fcc Ag−Co solid solution can be observed in the as-deposited $Co_{16}Ag_{84}$ nanowire arrays, the structure of the samples should be changed in the annealing process. As T_a is increased, only a relatively small change in $H_c \perp$ occurs initially, up to about $T_a = 300\,°C$, where an obvious steeper increase begins. This phenomenon is attributed to the appearance of small, single domain Co particles precipitated out of solid solution. Ultrafine ferromagnetic particles exhibit greatly enhanced coercivity because of their single-domain nature [15]. As T_a is further increased, the Co particles grow larger in size, further increasing $H_c \perp$. This trend continues until the critical size for single domain particles is exceeded. The maximum $H_c \perp$ is about 183 Oe at $T_a = 400\,°C$. However, the value of $H_c \perp$ decreases sharply as T_a is further increased beyond 400 °C. This may be attributed to either coalescence or contraction of the Co particles.

It should be noted that $H_c \parallel$ changes relatively little with increasing annealing temperature, as shown in Fig. 4, which is very different from the effect observed in the corresponding alloy films. This may be the result of a structural difference between the films and the arrays. It is known that Co particles can form and grow uniformly in all directions in the film during the annealing processes, which should contribute to both $H_c \perp$ and $H_c \parallel$. But the ordered $Co_{16}Ag_{84}$ nanowires in the AAM, with high aspect ratios (length to diameter, about 1000), have a highly anisotropic structure. Moreover, the alloy nanowires embedded in the AAM are separate from each other. Hence, the formation and growth of Co particles will be limited along the direction parallel to the nanowires in the annealing processes, which makes a large contribution to $H_c \perp$ but little contribution to $H_c \parallel$. Therefore alloy nanowire arrays with strongly anisotropic coercivity are obtained, and the coercivity can be optimized by choosing appropriate annealing conditions.

2.2.2 Saturation magnetization. Figure 5 shows the saturation magnetization (M_s) measured at room temperature as a function of annealing temperature for a sample of the ordered $Co_{16}Ag_{84}$ nanowire arrays of small and arbitrary mass. As T_a is increased, an increase in the saturation magnetization is detected, the maximum value measured at room temperature being 1.46 memu for $T_a = 500\,°C$. However, the value of the saturation magnetization decreases as T_a is further increased. The trend in M_s resulting from the changes in the Co particles during the annealing process is somewhat

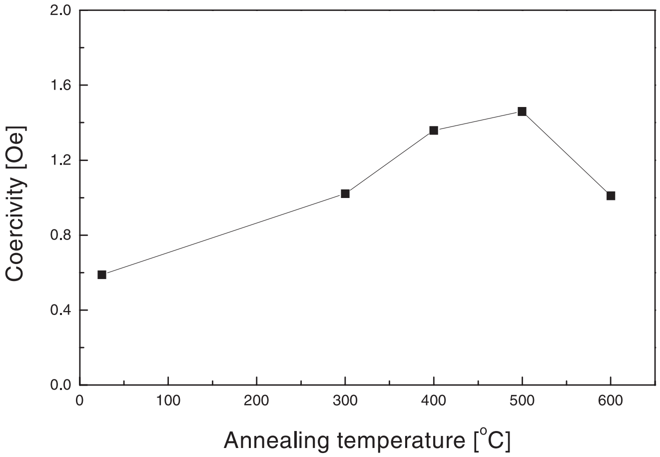

Fig. 5. Room-temperature saturation magnetization as a function of annealing temperature T_a

similar as that for the coercivity. However, their peak temperatures are different, 400 °C for $H_c \perp$ and 500 °C for M_s. In this regard, we think that the decrease in M_s begins just as the Co particles begin to coalesce or contact at higher temperature. Thus, $H_c \perp$ decreases as the critical size for Co particles is exceeded, but M_s continually increases until the Co particles coalesce or contact over 500 °C.

3 Conclusions

In conclusion, highly ordered $Co_{16}Ag_{84}$ alloy nanowire arrays were fabricated in AAMs using electrodeposition. The SEM, TEM and EDS observations show that the ordered $Co_{16}Ag_{84}$ alloy nanowire arrays were uniformly assembled into the hexagonally ordered nanochannels of the AAMs. It is found that their enhanced magnetic property is due to Co particles being precipitated out of the Co−Ag solid solution during the annealing process. The largely anisotropic magnetic properties of the ordered nanowire arrays can be obtained and optimized by choosing appropriate annealing conditions.

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