Fabrication of Numerous Ferromagnetic Metal Nanowires Using Electrodeposition Technique

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Abstract. To synthesize an array of numerous ferromagnetic nanowires, iron-group metals such as Ni, Co, Fe, Ni-Fe and Co-Fe alloys were electrodeposited from aqueous solution into a nanoporous template with numerical cylindrical nanochannels . The shape of nanowires was precisely transferred from the nanochannel template and the aspect ratio reached to around 150. Magnetic hysteresis loops revealed that Ni, Co and Fe nanowires were spontaneously magnetized to the long axis direction. Coercive force of the nanowires with 6000 nm in length was increased in decreasing the pore-diameter. The coercive force of Co nanowires with 40 nm in diameter has increased up to 1084 Oe.

Introduction

Nano-scale materials such as nanodots, nanosheets, nanotubes and nanowires show unique physical properties due to their quantum effects. Among of them, the array of numerous metallic nanowires with straight shape is the best candidate to be applied for magnetic storage media with high density domain. Metallic nanowires can be synthesized by stretching micro-scale metallic wires down to nano-scale, while the nanowires can be also synthesized by electrodeposition technique using a nano-well template such as an alumite film [1-8]. In 1975, using an anodic oxide coating film on aluminum, magnetic properties of electrodeposited Co nanowires and Co-Ni alloy nanowires were investigated by Kawai & Ueda [9]. In 1986, as an application to perpendicular magnetic recording medium, alumite films containing Fe nanowires were fabricated by Tsuya et al. [10]. In 1988, magnetization curling process in perpendicular direction was studied using Fe nanowire arrays in alumite media by Huysmans et al. [11]. In 1990, influence of the packing density on the magnetic behaviour was investigated using alumite media containing magnetic nanowires by Zhang et al. [12].
Flexible polymer films with numerous nanochannels such as ion-track etched polycarbonate membrane filters are also applicable to be used as a nano-well template. Flexible polymer films containing metallic nanowires would be novel electric devices such as printed circuit board (PCB). In this study, using an ion-track etched polycarbonate membrane filter with numerous cylindrical nanochannels, Iron-group metals such as Ni, Co, Fe, Ni-Fe and Co-Fe ferromagnetic alloy nanowires were synthesized by electrodeposition technique.

Experimental

Ion track-etched polycarbonate membrane filters with pore-diameter of 40, 80, 160 and 300 nm, pore-length of 6000 nm and pore-density of 10^8 pore•cm^{-2} were used as a template for growing metallic nanowires. On a surface of the membrane filter, a gold layer was sputter-deposited to cover the pores and make a cathode. Aqueous solution containing metal sulfate was used as electrolyte. To determine the optimum deposition potential for growing nanowires, cathodic polarizarion behavior was investigated in a wide range of cathode potential. Ni, Co, Fe, Ni-Fe and Co-Fe alloy nanowires were potentio-statically electrodeposited at 313 K. Composition of Ni-Fe and Co-Fe alloy electrodeposits were determined using EDX analysis. After growing the nanowires, the polycarbonate membrane filters were dissolved in organic solvent (dichloromethane and chloroform) and the

remains consisted of nanowires and a gold layer which served as a sample for SEM and TEM observation. Magnetic hysteresis loops of electrodeposited films and nanowires were obtained using vibrating sample magnetometer (VSM) with increasing the magnetic field up to 10 kOe.

Results and Discussions
1. Magnetic Alloy Films
Figure 1 shows the magnetic hysteresis loops of Ni, Co, Ni-22at.%Fe and Co-18at.%Fe alloy films electrodeposited on a copper foil. Magnetic field was applied to in-plane direction (//) and perpendicular direction ($\perp$) to the film plane. As shown in these figures, in perpendicular direction, the films were hardly magnetized. On the other hand, in-plane direction, the films were easily magnetized and the magnetization reached saturation at less than 1 kOe. Coercive force of Ni-22at.Fe and Co-18at.%Fe alloy films were several Oe, which is quite smaller than that of Ni and Co film (ca. 100 Oe). This is resulting from decreasing the magnetic anisotropy constant and magnetostriction constant of Ni and Co with increase in Fe content in Ni-Fe and Co-Fe alloy.
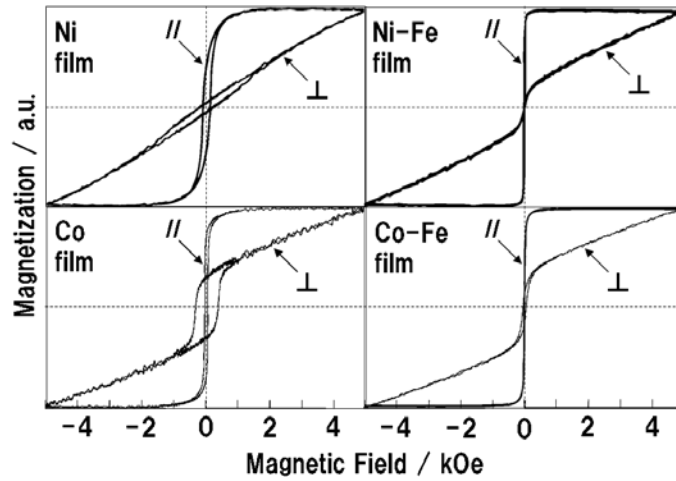

Figure 1 Magnetic hysteresis loops of Ni, Co, Ni-22at.%Fe and Co-18at.%Fe alloy films electrodeposited from aqueous solution.

Figure 2 shows the relationship between Fe content in Ni-Fe and Co-Fe alloy deposits ($R^{Fe/depo}$) and the coercive force obtained from magnetic hysteresis loops with the applied magnetic field of in-plane direction (//). With increase in Fe content in deposits, the coercive force decreased down to ca. several Oe level. It is well known that coercive force, H_c is expressed by the following equation if the rotation process is dominant in magnetization. $H_c = 2K/M_s$. Here, K and M_s mean magnetic anisotropy constant and saturate magnetization. Magnetic anisotropy constants of Ni, Co and Fe are as follows: K_{Ni} = -4.5 kJ/m^3 (-562.5 kGOe), K_{Co} = +530 kJ/m^3 (+66250 kGOe) and K_{Fe} = +48 kJ/m^3 (+6000 kGOe). Saturate magnetization of Ni, Co and Fe are as follows: M_{Ni} = 0.61 T (6100 G), M_{Co} = 1.79 T (17900 G) and M_{Fe} = 2.16 T (21600 G). Therefore, the theoretical coercive force of Ni, Co and Fe are estimated to be around 184 Oe (H_{Ni}), 7400 Oe (H_{Co}) and 555 Oe (H_{Fe}), which is larger than the value (ca. 100 Oe) obtained in this study. If the magnetic anisotropy constant and saturate magnetization of Ni-Fe and Co-Fe alloy can be expressed by the following equation, $K_{Ni(Co)-Fe}$ = $K_{Ni(Co)} \times (1- R^{Fe/depo}) + K_{Fe} \times R^{Fe/depo}$, $M_{Ni(Co)-Fe}$ = $M_{Ni(Co)} \times (1- R^{Fe/depo}) + M_{Fe} \times R^{Fe/depo}$, the estimated coercive force of Ni-Fe and Co-Fe alloy, $H_{Ni(Co)-Fe}$ will be expressed by the following equation, $H_{Ni(Co)-Fe} = 2K_{Ni(Co)-Fe}/M_{Ni(Co)-Fe}$. In this estimation, a Ni-9at.%Fe alloy will show minimum coercive force, which is almost zero, while the coercive force of Co-Fe alloy will decrease with increase in the Fe content. On the other hand, if the domain wall process is dominant in magnetization, H_c is expressed by the following equation. $H_c \propto \lambda\sigma/M_s$. The magnetostriction constants of Ni, Co and Fe are as follows: λ_{Ni} = -2.0$\times 10^{-5}$, λ_{Co} = -5.0$\times 10^{-5}$ and λ_{Fe} = +2.0$\times 10^{-5}$. If the magnetostriction constant of Ni-Fe and Co-Fe alloy can be expressed by the following equation, $\lambda_{Ni(Co)-Fe} = \lambda_{Ni(Co)} \times (1-$

$R^{Fe/depo}) + \lambda_{Fe} \times R^{Fe/depo}$, the estimated coercive force of Ni-Fe and Co-Fe alloy, $H_{Ni(Co)-Fe}$ will be expressed by the following equation, $H_{Ni(Co)-Fe} \propto \lambda_{Ni(Co)-Fe} \sigma / M_{Ni(Co)-Fe}$. In this estimation, Ni-50at.%Fe and Co-71at.%Fe alloy will show minimum coercive force, which is almost zero. In this study, as shown in Figure 2, the Ni-Fe and Co-Fe alloy films with low coercive force were obtained over the wide range of Fe content from 20 % to 60 %.
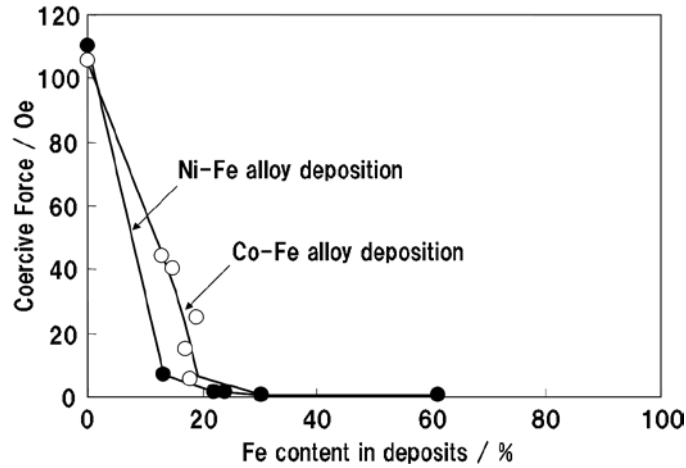

Figure 2 Relationship between Fe content in Ni-Fe and Co-Fe alloy deposits and the coercive force obtained from magnetic hysteresis loops of the alloy.

2. Magnetic Alloy Nanowires

Figure 3 shows the magnetic hysteresis loops of Ni, Co, Ni-22at.%Fe and Co-18at.%Fe alloy nanowires electrodeposited into polycarbonate templates with pore-diameter of 160 nm. Magnetic field was applied to in-plane direction (//) and perpendicular direction (⊥) to the membrane film plane. The perpendicular direction to the membrane film plane corresponds to the parallel direction to the long axis of nanowires. As shown in these figures, in perpendicular direction, the nanowires were easily magnetized and the magnetization reached to saturation at less than 2 kOe. Coercive force of Ni-22at.%Fe and Co-18at.%Fe alloy nanowires was ca. 200 Oe, which is almost same value to the Ni and Co nanowires (ca. 200 Oe) and the magnetic hysteresis loops show typical perpendicular magnetization behavior. This is resulting from the uni-axial magnetic anisotropy and single magnetic domain structure of the nanowires with large aspect ratio.
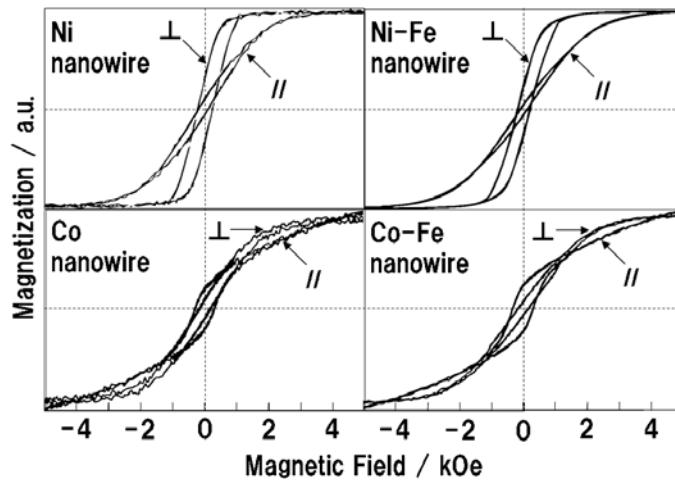

Figure 3 Magnetic hysteresis loops of Ni, Co, Ni-22at.%Fe and Co-18at.%Fe alloy nanowires electrodeposited from aqueous solutions.

Conclusions

The coercive force of Ni-22at.%Fe and Co-18at.%Fe alloy film was several Oe, which is much smaller than that of Ni and Co film (ca. 100 Oe). Ni-Fe and Co-Fe alloy films with low coercive force were obtained over the wide range of Fe content from 20 % to 60 %. The cylindrical shape was precisely transferred from the nanochannels to the nanowires and the aspect ratio reached up to ca. 60. Each nanowire consisted of a single domain. Basis on the uni-axial magnetic anisotropy and single magnetic domain structure of Ni, Co, Fe, Ni-Fe and Co-Fe alloy nanowires, the magnetic hysteresis loops showed typical perpendicular magnetization behavior and the coercive force reached to around 200 Oe.

Acknowledgements

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