Functional Nanowires Array Electrodeposited into Nanoporous Membrane Thin Films

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Abstract. Ni, Co, Fe and Co/Cu multilayered nanowires were electrodeposited into a nanowell template to synthesize novel functional ferromagnetic devices. Growth rate of Co/Co multilayered nanowires was around 40 nm•sec⁻¹ and the cylindrical shape was precisely transferred from the nanochannels to the nanowires and the aspect ratio reached up to ca. 150. Magnetic hysteresis loops of Ni, Co and Fe nanowires with diameter 40 nm showed typical perpendicular magnetization behavior due to the uni-axial shape anisotropy and the coercive force reached up to around 1 kOe. 2% of anisotropic magnetoresistance effect was observed in Ni nanowires electrodeposited into anodized aluminum oxide template, while 20% of giant magnetoresistance effect was observed in Co/Cu multilayered nanowires.

1. Introduction
One-dimensional nanowires with a large aspect ratio have received much attention due to their shape anisotropy and extremely large surface area [1-3]. Nanowires can be fabricated by manipulating metallic atoms one by one using scanning tunneling microscopy (STM) or stretching a micro-size wire down to nano-size, while they can be also prepared by electrochemically depositing metallic atoms into a nano-well template with numerous nanochannels [4, 5]. Nano-well templates such as anodized aluminum oxide films or polycarbonate membrane films with high density of nanochannels (about 10⁸~10¹⁰ cm⁻²) can be used in the template synthesis technique [6, 7]. Especially, Ni, Co and Fe nanowires array is the best candidate to be applied for magnetic storage media with high density domain, while Co/Cu multilayered nanowires array can be applied to magnetic field sensor with giant magnetoresistance property [8-10].

In this study, electrodeposition process of Ni, Co, Fe and Co/Cu multilayer into a nano-well template was investigated to synthesize novel functional ferromagnetic devices with anisotropic magnetoresistance and giant magnetoresistance property.

2. Experimental Procedures
Ion track-etched polycarbonate membrane films and anodized aluminum oxide films were used as a template for growing 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 (NiSO₄, CoSO₄, FeSO₄, CuSO₄, H₃BO₃, etc.) was used as electrolyte. To determine the optimum deposition potential for growing nanowires, cathodic polarization behavior was investigated in a wide range of
cathode potential. Co/Cu multilayered nanowires were electrodeposited by alternatingly changing the cathode potential from -0.6 V to -1.0 V. After growing the nanowires, the polycarbonate membrane films or anodized aluminum oxide films were dissolved in solvent and the remains consisted of nanowires and a gold layer which served as a sample for SEM observation. Magnetic hysteresis loops and magnetoresistive curves of electrodeposited nanowires were obtained using VSM with increasing the magnetic field up to 10 kOe.

3. Results and Discussion

Cathodic polarization curves for electrodeposition of Cu, Co and Ni are shown in Fig. 1. The equilibrium potentials of Cu and Co are estimated to be around +0.05 V and –0.48 V (vs.Ag/AgCl) on the basis of the Nernst equation. The cathodic current occurs at the potential region close to the equilibrium potential of Cu as shown in Fig. 1. It is well-known that Cu\(^{2+}\) ions begin to electrodeposit without an accompanying overpotential from the aqueous solution. Therefore, this cathodic current corresponds to the deposition current of Cu. With increasing cathodic current, at around 10\(^{-5}\)A, the potential significantly polarizes to the less-noble region. This phenomenon seems to be caused by the diffusion control of Cu\(^{2+}\) ions. In the potential region less-noble than the equilibrium potential of Co, the cathodic current increases again at circa –0.8 V. It is also well-known that the electrodeposition of iron-group metals such as Ni, Co, and Fe is accompanied by the overpotential due to the rate determining multi-step reduction mechanism. Therefore, this increase in cathodic current is mainly caused by the deposition current of Co. At the potential region less than –1.2 V, with increasing cathodic current, the potential polarizes significantly to be less-noble region due to the diffusion limit of Co\(^{2+}\) ions. Consequently, the optimum cathode potential for electrodeposition of Cu and Co can be determined to –0.6V and –1.0V.

Figure 1. Cathodic polarization curves for electrodeposition of Cu, Co and Ni from aqueous solutions.

Figure 2 shows effect of cathode potential on the time-dependence of cathodic current during electrodeposition of Co-Cu nanowires. To determine the growth rate of nanowires, the filling time of a nanochannel 6000 nm in length was estimated by monitoring the time-dependence of deposition current at each cathode potential as shown in Fig.2. When the nanochannels are filled and the nanowires reach the membrane surface, the current will increase drastically due to the formation of hemispherical caps. The growth rates were estimated by dividing channel length by channel-filling time. At –0.6 V, the filling time is around 300 s and the deposition rate is estimated to be about 20 nm
s\(^{-1}\), while the filling time is close to 30 s at –1.0 V and the deposition rate is estimated to be around 200 nm s\(^{-1}\). On the basis of the results shown in Fig.2, for example, Co (50nm)/Cu (50nm) multilayered nanowires can be electrodeposited by alternating the cathode potential from -0.6 V (2.5s for Cu layer) to -1.0 V (0.25s for Co-rich layer). However, in this process, deposited Co layer will dissolve during the Cu deposition. Therefore, Co deposition time should be adjusted longer than the estimated time. Figure 3 shows the time-dependence of cathodic current during electrodeposition of Co (50nm)/Cu (50nm) multilayered nanowires. Co deposition time was adjusted to 0.5s, which is two times of the estimation. The filling time is around 150 s and the deposition rate is estimated to be about 40 nm s\(^{-1}\).

Figure 2. Effect of cathode potential on the time-dependence of cathodic current during electrodeposition of Co-Cu nanowires.

Figure 3. Time-dependence of cathodic current during electrodeposition of Co/Cu multilayered nanowires.
SEM images of electrodeposited Co nanowires separated from polycarbonate membrane filters are shown in Fig. 4. The cylindrical shape was precisely transferred from the nanochannels to the nanowires and the aspect ratio reached up to ca. 150.

![Figure 4. SEM images of electrodeposited Co nanowires separated from polycarbonate membrane filters.](image)

Magnetic hysteresis loops of electrodeposited Ni, Co and Fe nanowires with diameter of 40 nm and length of 6000 nm are shown in Fig. 5. Magnetic field was applied to 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. These magnetic hysteresis loops show typical perpendicular magnetization behavior and coercive force of Co nanowires was ca. 1 kOe. This is resulting from the uni-axial magnetic anisotropy and single magnetic domain structure of the nanowires with large aspect ratio.

![Figure 5. Magnetic hysteresis loops of electrodeposited Ni, Co and Fe nanowires with diameter of 40 nm and length of 6000 nm.](image)

Magnetoresistive hysteresis of Ni nanowires electrodeposited into polycarbonate template (a) and anodized aluminum oxide template (b) are shown in Fig. 6. When the magnetic field was applied to perpendicular direction to the membrane film plane, the resistance was almost constant with increase in magnetic field. On the other hand, when the magnetic field was applied to in-plane direction to the membrane film plane, the resistance was decreased with increase in magnetic field and 2% of anisotropic magnetoresistance effect was observed in Ni nanowires electrodeposited into anodized aluminum oxide template.
Figure 6. Magnetoresistive hysteresis of Ni nanowires electrodeposited into polycarbonate template (a) and anodized aluminum oxide template (b).

Magnetoresistive hysteresis of Co/Cu multilayered nanowires electrodeposited into anodized aluminum oxide template (a) and polycarbonate template (b) are shown in Fig. 7. Independently of the magnetic field direction, the resistance was decreased with increase in magnetic field and 20% of giant magnetoresistance effect was observed in the multilayered nanowires with Co layer 10nm and Cu layer 10 nm electrodeposited anodized aluminum oxide template.

Figure 7. Magnetoresistive hysteresis of Co/Cu multilayered nanowires electrodeposited into polycarbonate template (a) and anodized aluminum oxide template (b).
4. Conclusions
Growth rate of Co/Co multilayered nanowires was around 40 nm·sec\(^{-1}\) and the cylindrical shape was precisely transferred from the nanochannels to the nanowires and the aspect ratio reached up to ca. 150. Magnetic hysteresis loops of Ni, Co and Fe nanowires with diameter 40 nm showed typical perpendicular magnetization behavior due to the uni-axial shape anisotropy and the coercive force reached up to around 1 kOe. 2% of anisotropic magnetoresistance effect was observed in Ni nanowires electrodeposited into anodized aluminum oxide template, while 20% of giant magnetoresistance effect was observed in Co/Cu multilayered nanowires.

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