Fabrication of Co/Cu Multilayered Nanowires Using a Pulsed Current Deposition Technique

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Abstract. Co/Cu multilayered nanowires with 40 nm in diameter were fabricated using a pulsed current deposition technique into a nanoporous template with numerous nanochannels. To determine the optimum electrodeposition condition of Cu and Co into the template, cathodic polarization behavior was examined at a wide range of cathode potential. Time-dependence of deposition current was monitored to determine the growth rate of Co and Cu nanowires. Co layer and Cu layer thicknesses were adjusted to several tens nanometers, by controlling the deposition times. With decreasing the each layer thickness, the coercive force of Co/Cu multilayered nanowires was decreased and the soft magnetic property was improved.

Introduction
One dimensional nanowires with a large aspect ratio have received much attention due to their shape anisotropy and extremely large surface area. This unique structure can be applied to develop the novel functional nano-materials such as electronic, magnetic and optical nano-scale devices. Metallic nanowires can be fabricated by manipulating metallic atoms one by one using a scanning tunneling microscope (STM) probe, while they can be also prepared by electrochemically depositing metallic atoms into a nanoporous template with numerous cylindrical nanopores [1-11]. In 1994, giant magnetoresistance (GMR) properties were found in Co/Cu multilayered nanowires electrodeposited in nanoporous polymer template by Piraux et al. [12]. In the report, magnetoresistance measurements with the current perpendicular to the layers were performed on the array of parallel nanowires. They observed a GMR of 15% at room temperature on Co/Cu multilayered nanowires. In the almost same time, GMR of nanowires with Co/Cu and Ni-Fe/Cu multilayers was demonstrated by Blondel et al. [13]. They made the multilayered nanowires with 6 µm long, 80 nm in diameter and each layer thickness of 5–10 nm in nanoporous polymer template. At ambient temperature, GMR of 14% for Co/Cu and of 10% for Ni-Fe/Cu was demonstrated in the current perpendicular to the layers.

In this study, Co/Cu multilayered nanowires with 40 nm in diameter were electrodeposited into ion-track etched polycarbonate membrane filters with numerical cylindrical nanochannels using a pulsed current deposition technique.

Experimental
Ion track-etched polycarbonate membrane filters with pore-diameter of 40 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 CoSO$_4$, CuSO$_4$ and H$_3$BO$_3$ was used as electrolyte. 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 filters were dissolved in organic solvent 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 nanowires were obtained using VSM with increasing the magnetic field up to 10 kOe.

Results and Discussions
1. Electrodeposition Process
For growing Cu and Co nanowires, cathode potentials were fixed to the range from -0.1 V to -1.1 V. 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.1. 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. Figure 2 shows the effect of cathode potential on the growth rate of Cu and Co nanowires. 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, Co/Cu multilayered nanowires were electrodeposited by alternating the cathode potential from -0.6 V (for Cu layer) to -1.0 V (for Co-rich layer).

Figure 1 Effect of cathode potential on the time-dependence of cathodic current during electrodeposition of Cu and Co nanowires.

Figure 2 Effect of cathode potential on the growth rate of Cu and Co nanowires electrodeposited into polycarbonate templates with channel-diameter of 40 nm.
2. Magnetic Property

Figure 3 shows the magnetic hysteresis loops of Co nanowires (a), Co(150nm)/Cu(150nm) multilayered nanowires (b) and Co(50nm)/Cu(50nm) multilayered nanowires (c) electrodeposited into polycarbonate templates with pore-diameter of 40 nm. 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. As shown in these figures, in perpendicular direction, the nanowires were easily magnetized and the magnetization reached to saturation at less than 3 kOe. Coercive force of Co nanowires (a) and Co(150nm)/Cu(150nm) multilayered nanowires (b) was ca. 1200 Oe, while the coercive force of Co(50nm)/Cu(50nm) multilayered nanowires (c) was almost half value to the Co nanowires. These 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 Co nanowires (a), Co(150nm)/Cu(150nm) (b) and Co(50nm)/Cu(50nm) (c) multilayered nanowires electrodeposited from aqueous solutions.

Figure 4 shows the relationship between Co layer thickness in Co/Cu multilayered nanowires and the coercive force obtained from the magnetic hysteresis loops. With decrease in Co layer thickness, the coercive force decreased down to ca. 200 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 saturated magnetization. The magnetic anisotropy constant of Co is as following. \( K_{Co} = +530 \text{ kJ/m}^3 (+66250 \text{ kGOe}) \). The saturated magnetization of Co is as following. \( M_{Co} = 1.79 \text{ T (17900 G)} \). Therefore, the coercive force of Co is estimated to be around 7400 Oe (\( H_{Co} \)), which is larger than the value (ca. 1200 Oe) obtained in this study. This is resulting from decreasing the magnetic anisotropy constant of Co due to Cu alloying effect in Co layer.
Figure 4 Relationship between Co layer thickness in Co/Cu multilayered nanowires and the coercive force obtained from the magnetic hysteresis loops.

Conclusions
Optimum deposition potentials of Cu and Co are determined to be about –0.6 and –1.0 V. Typical deposition rates of Cu and Co were roughly 20 nm s⁻¹ (at –0.6 V) and 200 nm s⁻¹ (at –1.0 V). Co/Cu multilayered nanowires were electrodeposited by alternatingly changing the cathode potential from -0.3 V to -1.0 V. With decreasing the each layer thickness, the coercive force of Co/Cu multilayered nanowires was decreased and the soft magnetic property was improved.

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References