ELECTRIC PROPERTIES OF COMPOSITION MODULATED NI-CO-CU PARTICLE AND MULTILAYER FILMS PRODUCED BY PULSE CONTROL ELECTROCHEMICAL DEPOSITION METHOD

C.S. Rizal*

Department of Electrical and Electronic Engineering

Muroran Institute of Technology, Mizumoto-cho, Muroran-shi,

Hokkaido, 050, Japan

This paper reports the investigation of the magneto-resistance (MR) effect and the film preparation conditions for the composition modulated Co-Ni-Cu alloy films produced by the pulse electrochemical deposition method. It was possible to produce multilayer films containing a Ni-rich layer with low coercive force, H_c, a Ni-Co layer with high H_c, and a non-magnetic Cu layer by controlling the step pulse potential from a single electrolyte containing Co, Ni, and Cu ions. The MR ratio observed in the film has a maximum value of 6% at 300 K. These films showed a highly sensitive change in the electrical resistance at a low magnetic field.

Keywords: pulse electrodeposition, electric resistance, multilayer films, Co-Ni

* Present address: Department of Electrical and Computer Engineering, The university of British Columbia, Room No.# 4060, 2332 Main Mall, Kaiser Building, Vancouver, V6T 1Z4, Tel: (604) 8273412, Fax: (604) 322-9030, E-mail: crizal@ece.ubc.ca

1. Introduction

Research on the physical properties of materials prepared in the nano-order scale has attracted attention in terms of new superior characteristics, which has not been known until recently. One of the examples is the multilayer film produced by alternately depositing different metals at the atomic level. Large magnetoresistance effects have been observed in the multilayer films composed of a ferromagnetic and a non-magnetic layer, and non-coupled multilayer films [1,2]. These discoveries have been for applications in magnetic field sensing. The production of such films has been carried out mainly by the vapor deposition method. We have been producing the multilayer films by pulse electrodeposition method [3,4]. Pulse electrochemical deposition is a useful technique with which it is possible to achieve atomic-scale control of the layer composition, thickness of the multilayer and the grain size in ferromagnetic films by regulating the pulse amplitude and width. The average film thickness is less than the atomic order, and is produced by reducing the intervals of the deposition time. The surface of the film with might not take a form of a uniform flat plane, and therefore, the film structure has a possibility of forming fine particles, a precipitated state or a non-equilibrium solid solution [5]. The surface form has a significant effect on magnetic characteristics such as a wide variation in coercive force, susceptibility, and magnetoresistance effect.

There are a few reports on magneto-transport properties and magnetism of granular alloy films produced by electrodeposition method [6-7], however, there have not been yet reports on the magnetoresistance effect of the non-magnetic coupling multilayer films and spin valve like films. In this study, multilayer films composed of a Co-rich layer with high coercive force, Ni-Co layer with low coercive force, and a nonmagnetic Cu layer are produced by controlling the step pulse potential from a single electrolytic solution containing Co, Ni and Cu ions. The relationship between magnetic field dependence of the magnetoresistance and the film structure of the composition modulated Ni-Cu-Co films yielded by pulse electrodeposition method is also studied.

2. Experimental Procedures

The electrolyte bath was composed of $NiSO_4.6H_2O$, $CoSO_4.7H_2O$, $CuSO_4.5H_2O$, H_3BO_3, and NaCl. Substrates were 15 nm copper thin films vapor deposited on glass plates. Multilayer films were deposited using a square pulse wave of current density 01 ~ 38 mA/cm^2. The pH value of 3.4 was maintained in the plating solution. The composition of the deposited films was determined by atomic absorption spectroscopy. MR ratio which is defined as MR%= [R(H)-R(H=0)]100% /R(H=0), is measured using a dc four probe method under the magnetic field up to 1kOe. Magnetic properties were investigated using a Vibrating Sample Magnetometer (VSM).

3. Experimental Result

3.1 Preparation of the ferromagnetic multilayer films by pulse electrodeposition

The relationship between the film composition and the current density in the electrodeposition was investigated in order to produce the multilayer films composed of more than two kinds of ferromagnetic layers with different magnetic characteristics.

Fig 1 shows the relationship between the composition of the electrodeposited films and the current density. A similar tendency was observed with the Fe-Ni-Cu film [8]. The concentration of $NiSO_4.6H_2O$, $CoSO_4.7H_2O$ and $CuSO_4$.5H2O in solution is 0.15mol/L, 0.03mol/L, and 0.005 mol/L, respectively. Film composition is close to 100% Cu at low current density of 0.15 mA/cm^2 as shown in Fig1. The composition ratio of the Ni and Co in the films can be changed mostly by the adjustment of the current density.

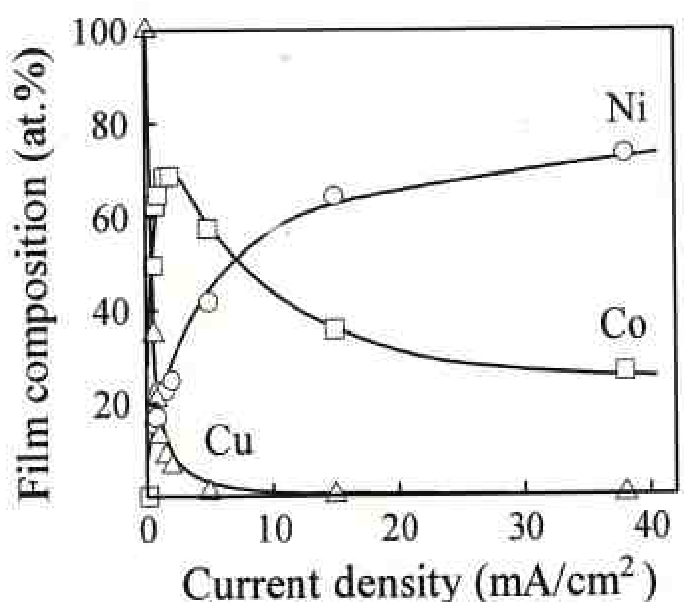

Fig. 1 Composition (Ni, Co and Cu at%) of the as a function of the current densities

Fig.2 shows the coercive force and magnetization curves of the multilayer films from Fig. 1 as a function of the current density. Inset in the upper right shows the corresponding magnetization curves. The coercive force shows a changing tendency with the variation of current densities.

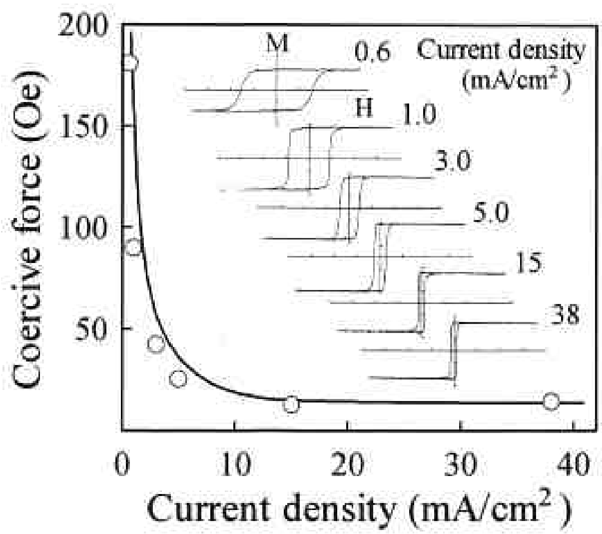

Fig. 2 Coercive force of the films from Fig. 1 as a function of the current densities and magnetization curves corresponding to the current densities

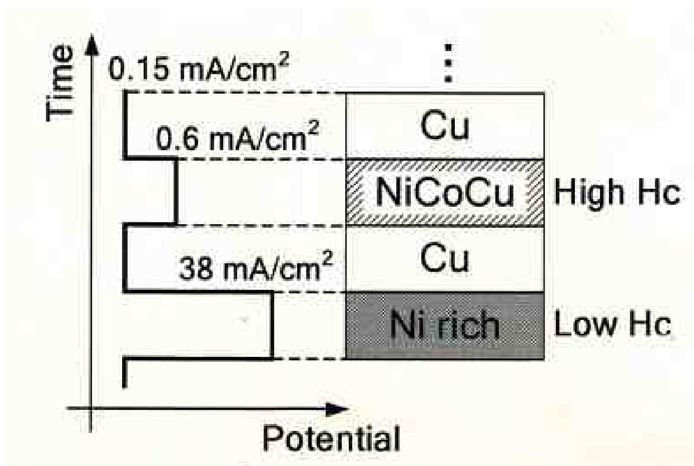

Fig.3 Relationship between the electrodeposition potential and multilayer structure of high H_c and low H_c films deposited at different current densities.

Fig. 3 shows a multilayer structure composed of non-magnetic Cu layer, $Ni_{16}Co_{50}Cu_{34}$ (ferromagnetic NiCoCu layer) having high coercive force, and $Ni_{74}Co_{26}$ (Ni-rich layer) having low coercive force deposited by using pulse wave with current densities of 0.15, 0.6, and 38 mA/cm2, respectively. Normally, the MR ratio of the multilayer films has been considered to be strongly depending on both the non-magnetic and magnetic layer thickness in the multilayer films.

Fig 4 shows the magnetic field dependence of MR ratio in the field region of ± 1kOe. MR ratio of Cu 9nm/NiCoCu 5nm/Cu 9nm/Ni-rich 5nm multilayer film changes abruptly at low magnetic field and it has a maximum value of is 3.5% at room temperature.

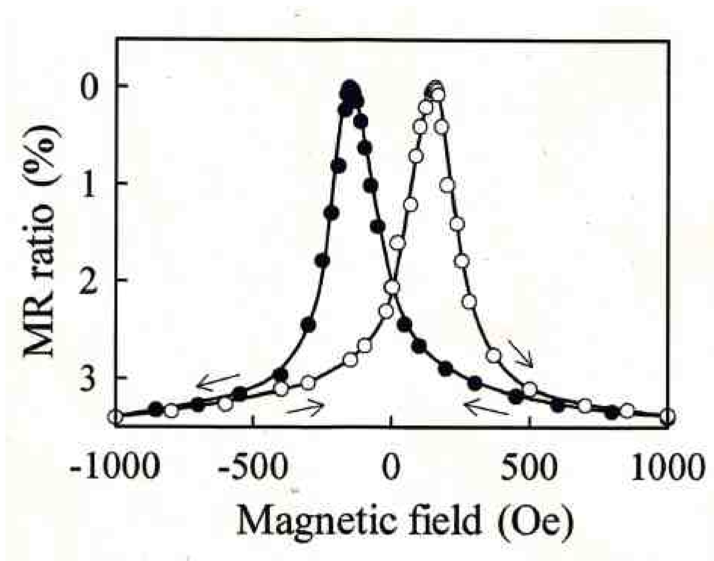

Fig. 4 The magnetic field dependence of the MR ratio for the [Ni-rich 5 nm/Cu 9 nm/NiCoCu 5 nm/Cu 9 nm]$_5$ films

3.2 Electric properties of composition modulated multilayer films produced by reducing sweep time of the deposition pulse

Generally, the magnetic characteristics of the thin films strongly depend on the film composition, crystal state, and precipitated state in the granular fine particle [9]. If the sweep time of the periodic pulse during the pulse electrodeposition is made very short, or the average layer thickness is reduced to less than an atomic layer, the layer structure has the possibility of forming the fine particle, precipitated or non-equilibrium solid solution. Eventually, it leads to the production of the supersaturated solid solution in the non-equilibrium state, and therefore, affects the magnetic characteristics, such as permeability and coercive forces [10].

Fig 5 (a) shows a Cu/[CoNiCu/Cu]$_N$/Ni-rich multilayer structure with three layers; NiCoCu/Cu with high coercive force, Ni-rich layer with low coercive force, and non-magnetic Cu layer. To produce a layer with higher coercive force, the single CoNiCu layer of Fig. 3 is replaced with a series of [Cu/NiCoCu]$_N$ by changing the sweep time of the deposition pulse.

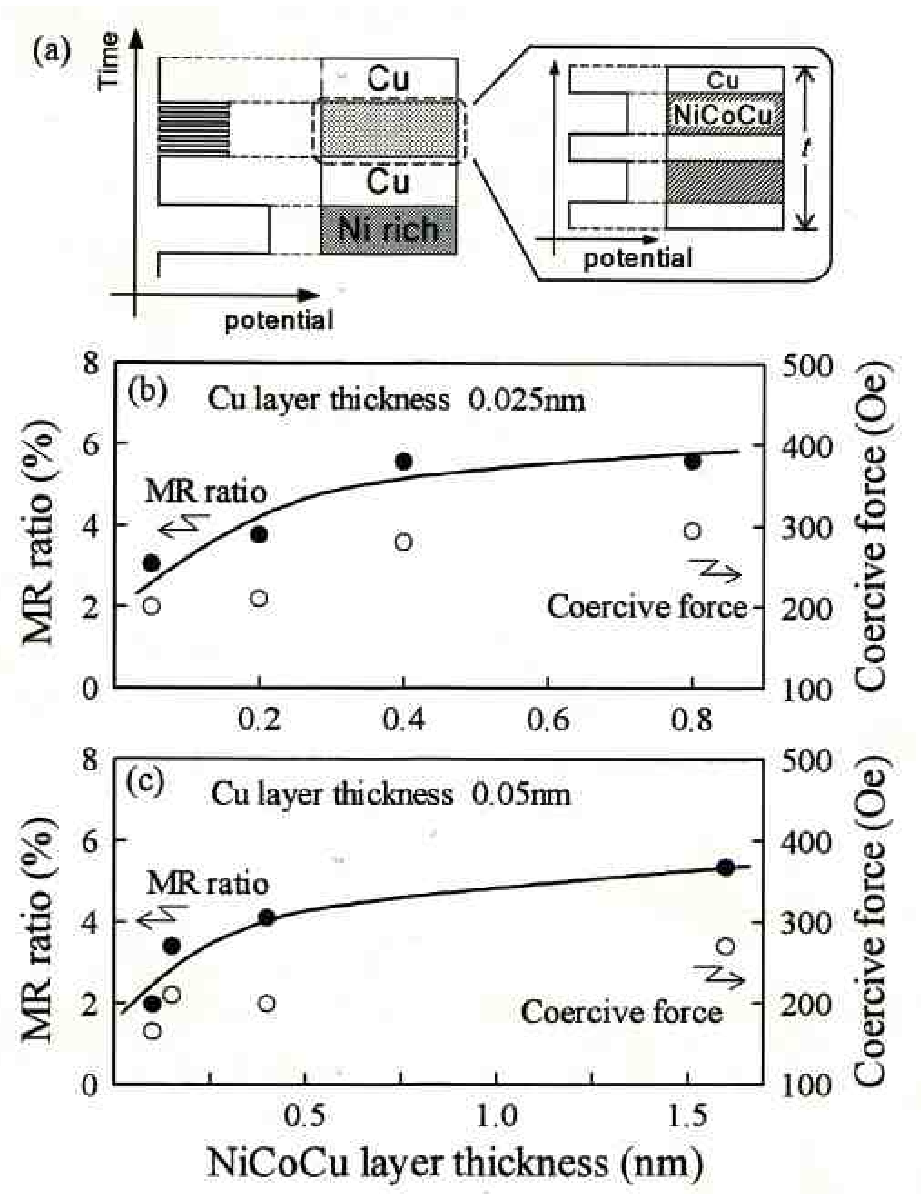

Fig. 5 Schematic illustration of the (a) ferromagnetic multilayer films with thinner layers produced by reducing the time interval of deposition pulse, (b) and (c) the coercive force of the [NiCoCu/Cu] films and the MR ratio of the films [Ni-rich 5 nm/Cu 9 nm/(NiCoCu/Cu) 5 nm/Cu 9 nm]$_5$

The Cu layer thickness is kept constant each at 0.025 and 0.5 nm. The stacking number, N is varied to keep the total ferromagnetic layer thickness to 5 nm. The average layer thickness values are estimated from both the deposition time and the current densities. MR ratio of the new composition modulated multilayer structure is measured. Interestingly, not only is the coercive force of CoNiCu/Cu layer increased, but also the magnetoresistance of the multilayer film increased to 6% as shown in Fig. 5(b) and (c). Thus, multilayer films with varying values of coercivity are useful for devices requiring a high MR ratio and a high coercive force.

Acknowledgement:

Many thanks to Prof. Lukas Chrostowski, Dept. of Electrical and Computer Engineering, the University of British Columbia, Canada for his fruitful comments and feedback. The work was partially supported by the Ministry of Science and Culture, Japan (Monbukagakusho).

References

[1] M.N. Baibich, J.M. Broto, A. Fert, F. Nguter Van Dan, F. Petroff, P. Eitienne, G. Greutet, A. Friederich and J. Chazelas, J. Phys. Rev. Lett. 61 (1988) 2472.

[2] S.S. P. Parkin, R. Bhadra, and K.P. Roche, J. Phys. Rev. Lett., 66 (1991).

[3] T. Houga, A. Yamada, and Y. Ueda, J. Japan Inst. Metals, 64 (2000) 739

[4] C.L.S. Rizal, A. Yamada, Y. Ueda, Int. Conference on Magnetic Film and Surface, ICMFS (2002) 303

[5] Y. Ueda, M. Ito, J. Appl. Phys, Jpn, 33 (1994) 1403

[6] S. Kainuma, S. Ishikura, and, K. Hisatake, J. Magn. Soc. Jpn., 21 (1997) 557

[7] J. Q. Wang and G. Xiao, Phys. Rev. B 49, 3982–3996 (1994)

[8] A. Yamada, M. Shirota, C. L. S. Rizal, T. Houga, and Y.Ueda, J. Japan Inst. Metals, Vol. 66, No. 9 (2002), pp. 869-872

[9] D. Altbir, J. Castro, P. Vargas Phys. Rev. B 54, R6823–R6826 (1996)

[10] C.O. Tiller and G.W. Clark, Phys. Rev. Lett., 110 (1958) 583

