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Electrodeposition of GMR Ni/Cu Multilayers in a Recirculating Electrochemical Flow Reactor

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Abstracts The recirculating electrochemical flow reactor developed at UCLA has been employed to fabricate nanostructured GMR multilayers. For comparison, Ni/Cu multilayers have been electrodeposited from a single bath, from dual baths and from the recirculating electrochemical flow reactor. For a magnetic field of 1.5 kOe, higher GMR (Max. -5%) Ni/Cu multilayers with low electrical resistivity ($< 10\ \mu\Omega\cdot cm$) were achieved by the electrochemical flow reactor system than by the dual bath (Max. GMR = -4.2% and $< 20\ \mu\Omega\cdot cm$) or the single bath (Max. GMR = -2.1% and $< 90\ \mu\Omega\cdot cm$) techniques. Higher GMR effects have been obtained by producing smoother, contiguous layers at lower current densities and by the elimination of oxide film formation by conducting deposition under an inert gas environment. Our preliminary GMR measurements of Ni/Cu multilayers from the electrochemical flow reactor obtained at low magnetic field of 0.15 T, which may approach or exceed the highest reported results (-7% GMR) at magnetic fields > 5 kOe.

Key words GMR, Ni/Cu multilayer, recirculating electrochemical flow reactor, electrodeposition.

1. Introduction

There is considerable interest in the fabrication of nano-dimensional multilayer structured films and high performance hard magnetic thin films for new microelectronic devices. Giant magnetoresistance (GMR) materials have potential applications in sensor and computer technologies based on unique properties, including the change of electrical resistance in response to a magnetic field.[1,2]

Electrodeposition is a versatile and inexpensive technology to fabricate soft magnetic and nanostructured thin films. Electrodeposition has a number of advantages over other deposition technologies: less costly, easy scale up and maintainance, and relatively low temperature (room) operating conditions. Dini claimed that physical deposition techniques may be higher at least ten times in cost compared to electrodeposition methods.[3] Furthermore, Schindler et al. reported that high quality thin film magnetic electrodeposits can be produced under conditions equivalent to a vacuum deposition condition of 5×10^{-10} mbar.[4]

In the fabrication of nanostructured GMR multilayers, the single bath technique (alternating deposition potentials or current densities) is extensively used because of its simplicity.[5] However, the two metals (nonmagnetic-magnetic) codeposit during the deposition of the less noble metal, resulting in lower GMR effects. The amount of the more noble (nonmagnetic) metal codeposited with the less noble (magnetic) metal can be minimized, but not eliminated completely, by increasing the ratio of less noble to more noble metal ions in the bath. In addition, the single bath technique is limited to a few selected multilayer combinations due to the requirement of compatibility of the components in the plating solution. With the dual bath technique the magnetic and nonmagnetic components in the plating solutions do not have to be compatible, because multilayers are obtained by repeatedly transferring the substrate between two different electrolytes, alternately electrodepositing the magnetic and nonmagnetic films.[6] However, the deposition procedure is tedious and undesirable oxides at the nonmagnetic-magnetic interfaces can form during the transfer and rinsing steps.

A novel reactor system has been developed at UCLA to electrodeposit high performance hard magnetic thin films and GMR multilayers without the disadvantages of the single and dual bath methods.[7,8] This new process employs a recirculating electrochemical flow reactor, wherein multilayers are electrodeposited under an inert atmosphere. Electrodeposition under an inert gas environment and applying a small cathodic current during rinsing steps precludes interfacial oxdie formation. The electrical resistivity and GMR properties of multilayer deposits

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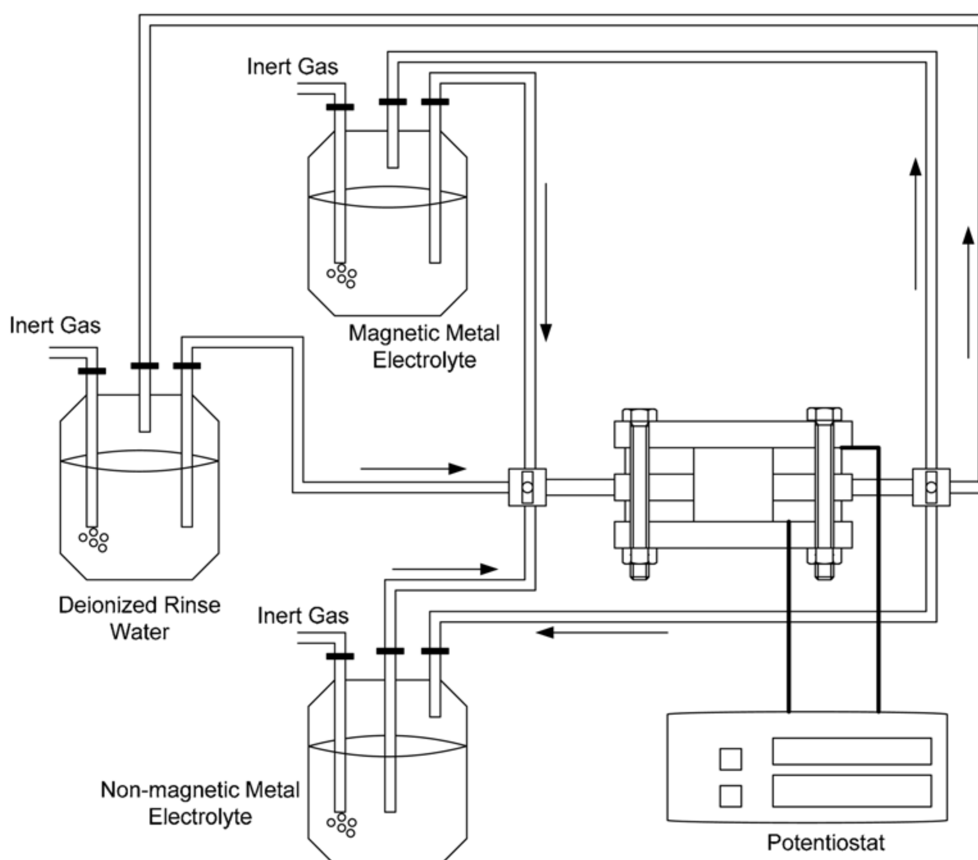

Fig. 1. Schematic of the recirculating electrochemical flow reactor.

fabricated by single bath, dual bath and the recirculating electrochemical flow reactor are compared.

2. Experimental procedure

Ni/Cu multilayers have been electrodeposited by the three deposition methods. GMR effects and electrical resistivity have been measured at varying Ni and Cu layer thicknesses.

In the single bath technique, multilayers were obtainted by applying potential pulses. The thickness and composition of magnetic and nonmagnetic layers were controlled by the applied potential and time. The deposition potential for Ni and Cu were -1.2 and -0.7 V vs. SCE (saturated calomel electrode), respectively. The nickel sulfamate-copper sulfate plating solution (1.5 M $Ni(H_2NSO_3)_2$ + 0.0157 M $CuSO_4$ + 0.5 M H_3BO_3) at pH 4 was selected, based on the work of other investigators.[9-10)]

In the dual bath technique, multilayers were deposited by transfering the substrate between two different electrolytes. Because the dual bath technique has much more flexibility for choosing plating solutions, nickel chloride and acid copper sulfate plating solutions were chosen because nano-thick films from these plating solutions were smooth and contiguous. The composition of nickel and copper plating solutions were 0.2 M $NiCl_2$ + 0.7 M NaCl + 0.5 M H_3BO_3 + 0.0075 M Saccharin and 0.8 M $CuSO_4$ + 0.5 M H_2SO_4 + Brightener, respectively. Electrodeposition was performed under a constant current density of 5 mA/cm^2 at room temperature. Individual layer thicknesses were controlled by the charge passed.

The recirculating electrochemical flow reactor consists of the reactor, potentiostat, pumps, two 3-way switches and three reservoirs (Fig. 1). Reservoirs contained a plating solution for a magnetic metal, a plating solution for the nonmagnetic metal, and deionized rinse water, repectively.

The electrodeposition of GMR multilayers in the recirculating electrochemical flow reactor differed from the dual bath method because the former was produced in a controlled inert environment. Ultra high purity argon gas (99.999%) was used to sparge the reservoirs and to facilitate flow of the plating solutions through the reactor instead of transferring the substrate between electrolytes.

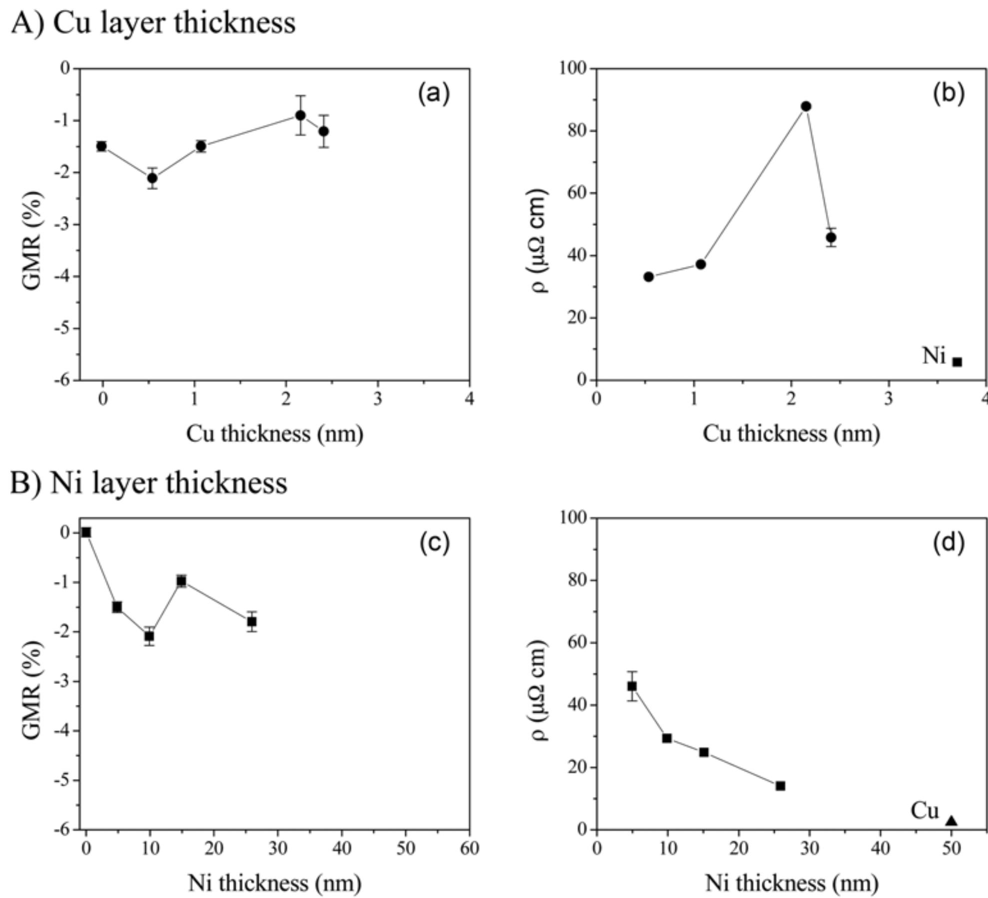

Fig. 2. The effect of layer thickness fabricated by single bath technique on GMR (a, c) and electrical resistivity (b, d) : A) nickel layer thicknesses = 5 nm and B) copper layer thicknesses = 2.7 nm.

The plating sequence was as follows: one layer is electrodeposited by recirculating its plating solution through the reactor. When the deposition is completed, the valve is switched and deionized water is pumped through the reactor to displace the remaining plating solutions; a low cathodic current is applied to the substrate to preclude oxidation of the film during the rinsing step. After rinsing, the other plating solution is recirculated through the reactor, and the second film is electrodeposited. This is followed by another rinsing step. Multilayer films are deposited by repetitive cycling.

There are two type of GMR measurements: 1) the applied current parallel to the plane of the layers (CIP-MR), 2) the applied current perpendicular to the plane of the layers (CPP-MR). In these studies, CIP-MR was measured by the standard four point probe dc current technique at room temperature with an applied magnetic field of 1.5 kOe which was not sufficient to saturate the Ni/Cu multilayers; larger GMR effect can be expected at higher magnetic field.

3. Results and Discussion

Magnetoresistance is the change of electrical resistance due to the presence of an external magnetic field. It is believed that the GMR effect results from a change in the magnetic moment of alternating magnetic layers from antiferromagnetic to ferromagnetic coupling in the presence of an external magnetic field; it decreases as the adjacent Cu layer thickness increases due to weaker coupling of the magnetic layers. GMR is dependent on the strength of the external magnetic field and temperature, and also on the direction between the applied magnetic field and the applied current.

Ni/Cu multilayers were electrodeposited by three deposition procedures (single bath, dual bath and the recirculating electrochemical flow reactor) to compare the GMR effect.

3.1 Single bath technique

Fig. 2a shows the effect of varying copper layer thickness from 0.5 to 2.7 nm at constant nickel layer thickness of

5 nm on the electrical resistivity and the GMR effect. The electrical resistivity increased then decreased with a maximum of 88 μΩ·cm at 2 nm Cu. MR also increased, then decreased from -2.1 to -0.9% with maximum at 0.6 nm Cu. The maximum applied magnetic field was 1.5 kOe. Lashmore et al. observed oscillatory GMR behavior with a maximum of -3.4% at 0.9 nm Cu at constant nickel layer thickness of 2 nm with an applied magnetic field 5 kOe.[11] Toth et al. show maximum GMR of -2.8% at 1.5 nm Cu with 8 kOe.[12] The maximum GMR of -7% at 0.7 nm Cu with applied field of 8 kOe was reported by Bird and Schlesinger for electrodeposited Ni/Cu multilayers.[13] This value is greater than sputtered Ni/Cu multilayers (-5.6%).[14] Our lower GMR (-2.1%) of deposits from the single bath compared to theirs is attributed to the lower applied field of 1.5 kOe, which is not sufficient to saturate the Ni/Cu multilayers. There appears to be a significant 33% increase in the GMR value when the external magnetic field increased from 1.5 to 8 kOe.[15]

Electrical resistivity of multilayers deposited from the single bath is much higher than electrodeposited pure Cu and Ni films. Similar trends have been observed by Menezes and Anderson with maximum electrical resistivity at 2 nm Cu.[16] Higher electrical resistivity might be attributed to codeposition of Cu in the nickel layers; bulk NiCu alloys exhibit increased elecrical resistivity from 5.5 to 50 μΩ·cm with increased Cu content from 0 to 50% Cu.[17,18] Copper content in the magnetic layers of Ni/Cu multilayers from single bath deposition can be as high as 10%, based on DC plating. Rougher interfaces due to low copper concentrations (0.0157 M) in the plating solution could also result in an increase in electrical resistivity. Under these conditions, copper is electrodeposited under mass transfer control and the more negative copper deopsition potentials (-0.4 to -0.8 V) results in three-dimensional rather than two-dimensional films.

Fig. 2b shows the dependence of electrical resistivity and magnetoresistance of Ni/Cu multilayers on nickel layer thickness with the copper layer thickness fixed at 2.7 nm. The electrical resistivity monotonically decreased from 46 to 14 μΩ·cm as the Ni layer thickness increased from 5 to 26 nm while magnetoresistivity oscillated between -1.0 and

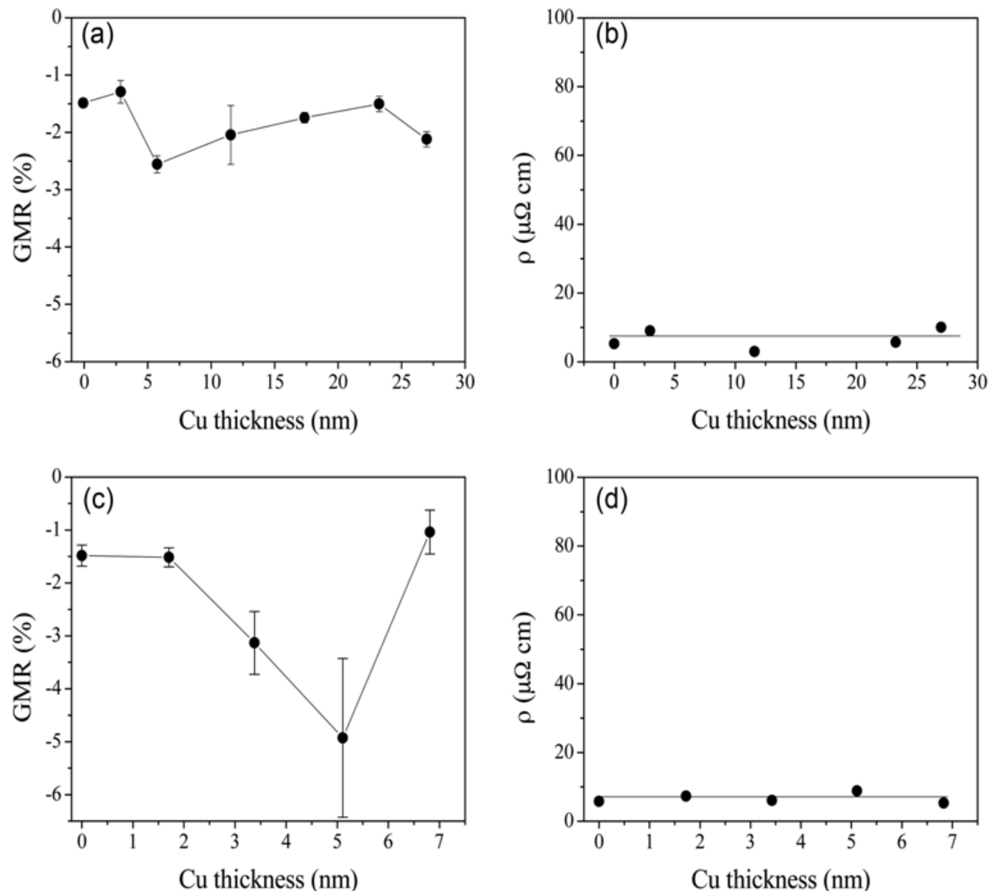

Fig. 3. The effect of Cu layer thickness on GMR and electrical resistivity fabricated by (a, b) dual bath and (c, d) electrochemical flow reactor techniques. Nickel layer thicknesses is 57 nm.

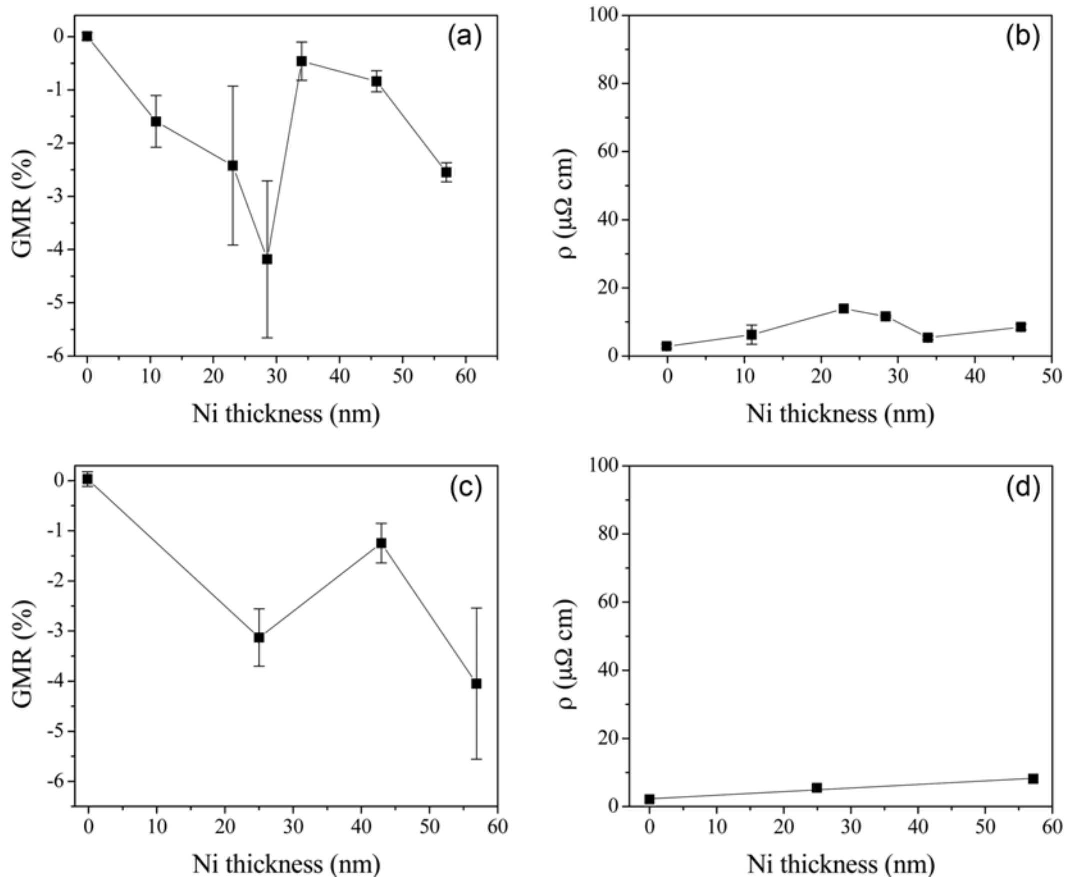

Fig. 4. The effect of Ni layer thickness on GMR and electrical resistivity fabricated by (a, b) dual bath and (c, d) electrochemical flow reactor. Copper layer thicknesses is 5 nm.

-2.1%. The maximum GMR effect was observed when the nickel layer thickness was 10 nm. Bakonyi et al. electrodeposited Ni/Cu multilayers from a sulfate bath and observed maximum GMR of -2% at 2 to 3 nm nickel layer thickness; electrical resistivity decreased slightly from 50 to 40 μΩ·cm as the nickel layer thickness increased from 1 to 10 nm, while the copper layer thickness was kept at 0.7 nm.[19)]

3.2 Dual bath technique

Fig. 3a shows the change in the electrical resistivity and the GMR effect as copper layer thicknesses are varied up to 30 nm, keeping the nickel layer thickness constant at 57 nm. The electrical resistivity (≈ 10 μΩ·cm) was independent of copper layer thickness and a maximum GMR of -2.9% was obtained at 5 nm Cu. Compared to Ni/Cu multilayers deposited with the single bath technique, the electrical resistivity was significantly lower. Blondel, Doudin and Ansermet studied single bath and dual bath techniques on electrodeposited Co/Cu multilayers and obtained lower electrical resistance with multilayers using the dual bath technique.[20)] They attributed the lower electrical resistivity to lower interfacial resistivity between magnetic and nonmagnetic layers.

Fig. 4a shows the dependence of electrical resistivities and magnetoresistances of Ni/Cu multilayers on the nickel layer thickness, while the copper layer thickness was fixed at 5 nm. The electrical resistivity (< 20 μΩ·cm) was independent of Ni layer thickness from 10 to 60 nm, while the magnetoresistivity oscillated between -1.8 and -4.2%. The maximum GMR effect was observed for a nickel layer thickness of 30 nm.

3.3 Recirculating electrochemical flow reactor

Fig. 3b shows the effect of copper layer thickness on the electrical resistivity and GMR effect for copper layer thickness varying up to 7 nm, while keeping constant the nickel layer thickness of 57 nm. The electrical resistivity (≈ 10 μΩ·cm) was independent of copper layer thickness similar to deposits obtained with the dual bath technique; however, a maximum GMR of -5% compared to -2.9% for

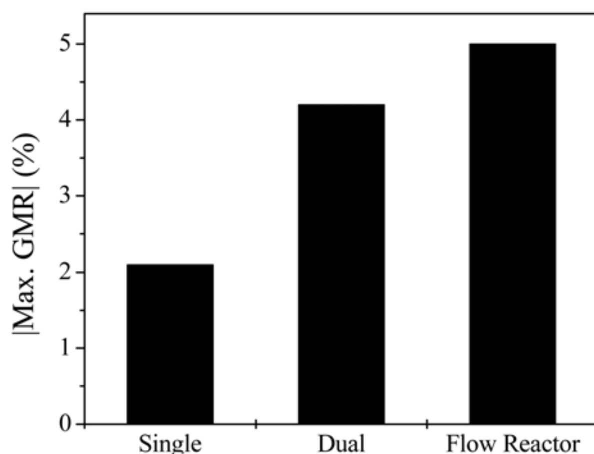

Fig. 5. Maximum GMR effect of Ni/Cu multilayers prepared by three electrodeposition techniques.

the dual bath deposits was obtained at 5 nm Cu. As indicated above, GMR is dependent on the external magnetic field.[9] Because our applied magnetic field limitation was much lower than that used by others, Ni/Cu multilayers deposited from the electrochemical flow reactor may approach the highest reported value of -7% at 8 kOe.

Fig. 4b shows the dependence of electrical resistivity and magnetoresistance of Ni/Cu multilayers deposited in the electrochemical flow reactor on the nickel layer thickness, while the copper layer thickness was fixed at 5 nm. Electrical resistivity increased slightly (to 10 μΩ·cm) as the Ni layer thickness increased to 57 nm; magnetoresistivity oscillated between -1.5 and -4.2%. The maximum GMR effect was observed for a nickel layer thickness of 25 nm. The electrical resistivity was substantially lower than Ni/Cu multilayers deposited with the single bath technique. It might be attributed to the elimination of copper in the Ni layers and oxide film formation at the interfaces, resulting smoother layer with well defined interfaces.

Fig. 5 shows the maximum GMR effects of Ni/Cu multilayers prepared by the three different electrodeposition technique. Using the same solution compositions and deposition current densities, approximately 20% increase in the maximum GMR effect was achieved with the electrochemical flow reactor compare to the dual bath approach (-5% vs. -4.2%). The GMR effect for deposits from single baths containing dilute $CuSO_4$ concentration was considerably lower (-2.1%). As indicated above, the greater GMR effect of multilayers prepared by the recirculating electrochemical flow reactor is ascribed to smoother layers and the absence of interfacial oxides.

4. Conclusion

Ni/Cu multilayers have been fabricated by three electrodeposition techniques: single bath, dual bath, and the recirculating electrochemical flow reactor. Greater GMR (-5%) Ni/Cu multilayers with low electrical resistivity (< 10 μΩ·cm) have been prepared using the recirculating electrochemical flow reactor than by either dual bath (Max. GMR = -4.2% and < 20 μΩ·cm) and single bath (Max. GMR = -2.1% and 10 to 90 μΩ·cm) technique under a magnetic field of 1.5 kOe. The greater GMR effect is attributed to smoother interfaces and the absence of interfacial oxides. Ni/Cu multilayers prepared by the electrochemical flow reactor show a promise to provide superior GMR effects to those prepared by vacuum deposition method, e.g. sputtering (Max. GMR - -5.6%). This results illustrate the effectiveness of our electrochemical flow reactor system for the electrodeposition of GMR multilayer over single and dual bath techniques. Other nonmagnetic-magnetic combinations, (e.g., Co/Cu, CoNi/Cu, NiFe/Cu, CoFe/Cu, CoNiFe/Cu) can be fabricated using our recirculating electrochemical flow reactor to produce higher performance GMR nanostructured multilayers.

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