DESIGN AND FABRICATION OF NANOMAGNETIC SENSORS BASED ON ELECTRODEPOSITED GMR MATERIALS

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Abstract

The operation of magnetic sensors is based on different physical principles, leading to the fabrication of different magnetic sensor types. Commercially available magnetic sensors such as Hall effect devices, inductive coil and fluxgate magnetometers have their own advantages and limitations. Magnetoresistive sensors are based on the change of the electric resistivity when they are subjected to a magnetic field. We introduce a low-cost method i.e. electrodeposition of magnetic multilayers, in order to fabricate sensitive magnetic sensors. We have successfully grown Co/Cu and Ni/Cu multilayers on n-type (100) Si substrate, from a single electrochemical electrolyte containing either both (Co$^{2+}$ and Cu$^{2+}$) or both (Ni$^{2+}$ and Cu$^{2+}$) ions, for growing Co/Cu and Ni/Cu multilayers respectively. While a maximum change of 12 percent was observed in the electric resistivity of the Co/Cu films when they were subjected to a magnetic field of 2000 Oe, the maximum change in resistivity for Ni/Cu multilayers was only 3.5 percent. Nevertheless, the sensitivity of multilayer Ni/Cu films in low magnetic fields (up to 100 Oe) was found to be almost twice that obtained for Co/Cu films.

Keywords: electrodeposition, magnetic sensors, multilayer thin films.

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1. Introduction

Since the very first observation of giant magnetoresistance (GMR) in Fe/Cr multilayer films with antiferromagnetic coupling between adjacent Fe layers in 1989 [1], much attention has been paid to multilayers consisting of alternating layers of a ferromagnetic metal e.g.: Fe, Ni, Co or their alloys and a non-magnetic transition or noble metal e.g.: Ag, Cu, Pt etc., because they can exhibit special properties such as the magneto-optic Kerr effect (MOKE), anisotropic magnetoresistance (AMR) and giant magnetoresistance. The effect of GMR in Fe/Cr multilayers is much stronger than the usual AMR, measured for a single Fe layer with the same thickness, which was prepared in similar growth conditions in order to enable comparison.

The study of magnetic multilayer films is of interest as they exhibit GMR with application in data storage technology and magnetic sensing. The properties of multilayers are strongly dependent on the layer thicknesses and effects of the boundaries between magnetic and non-magnetic layers. Multilayer thin films usually consist of layers with thicknesses from a few angstroms up to ~100 Å. The mechanical, transport and magnetic properties of multilayer thin films are often radically different from the bulk properties of their constituents.

Thin films are most commonly prepared by vacuum base techniques such as evaporation, sputtering and molecular beam epitaxy (MBE). In these techniques a material (metal, alloy or semiconductor) is evaporated or sputtered and deposited on a substrate to form a thin film. In MBE, under certain conditions, it is possible to grow one atomic layer after another, forming a nearly perfect single crystal with very smooth surface and sharp interface. However, the
required equipment is complicated and expensive. Sputtering, which is less complicated and less expensive, has been widely used to produce thin films and multilayers, although the produced materials are not perfect single crystals and do not always have a smooth surface or very sharp interfaces.

Electrodeposition as an alternative deposition technique is economically important because of its low cost and flexibility. It is an inexpensive and versatile method of preparing thin metal films that, unlike most alternatives, does not require a vacuum system. For example, electrodeposited Cu is now the material of choice for the interconnects in ultra large scale integrated (ULSI) circuits [2], while electrodeposited soft magnetic alloys are an important component of magnetic recording heads.

In spite of having some advantages over the vacuum based techniques, electrodeposition can only take place when there is a conducting path to the external circuit, hence just metallic or semiconductor materials can be used as substrates. However, this can also be considered as an advantage of electrodeposition to be a selective method: when a conducting substrate is covered by a patterned resist layer, deposition occurs only where the substrate is exposed. This is particularly important for high-aspect ratio features, because deposition on the resist, which is unavoidable (e.g. in the case of metal evaporation) can easily block them. In our previous work we took advantage of the selectivity of electrodeposition to prepare Co/Pt multilayers in nano-porous track-etched polycarbonate membranes, producing multilayered nanowires with diameters of a few tens of nm and lengths of several μm [3].

Electrodeposition usually refers to deposition of a metal or an alloy from an electrolyte by passing a charge between the two electrodes located in the electrolyte. If an external power supply drives a current through the cell, metal ions are reduced to metal atoms at one of the electrodes known as the cathode. The cathode forms the substrate of the electrodeposited film, and is also referred to as the working electrode. To complete the circuit, an oxidation reaction takes place at the second electrode, known as anode or secondary electrode. Electrodeposition also refers to as potentiostatic or galvanostatic control depending on whether the external power supply is used to fix the potential applied to the substrate or the current passing through it. The deposition rate for a given electrode depends on the cathode potential (or current density) so that the more negative the cathode potential (or current density), the faster the electrochemical reaction, and therefore, the higher the deposition rate. Fig.1 shows a cell containing an electrolyte and three electrodes connected to a potentiostat. A computer-controlled potentiostat applies a potential difference between the working electrode (WE) and the reference electrode (RE). Since the RE is at fixed potential relative to the solution, any change in the potential applied to the working electrode changes the WE potential relative to the solution by the same amount.

The working electrode is the substrate (a metal or a semiconductor) on which the desired material is subsequently deposited. The choice of electrode material is determined by the nature of the material deposited. The secondary electrode (SE) supplies the current required by the WE. It can be any non-polarizable metal or other conductor that has no chemical reaction with the electrolyte. It is located far from the WE to give as uniform a current distribution as possible across the cell in order to give uniform deposition.

Despite the simplicity of the experimental set up and low cost, the phenomenon of electrodeposition is very complex, since it is typically a non-equilibrium growth process and it involves so many variables such as electrolyte pH and concentration, cation diffusion, and type of substrate.
2. Electrodeposition of Multilayers and Superlattices

One approach in developing materials with new physical properties is to artificially structure the materials; an easy way to do this is by layering them and making a sandwich or multilayer structure rather than homogenous alloys.

Multilayer thin films consist of successive layers of two or more different materials deposited on a substrate. The thickness of each layer is typically between a few angströms and hundreds of angströms and the multilayer may contain up to several hundred layers. A superlattice is a periodic multilayer. Superlattices have been widely studied because their properties may be different from bulk materials.

MBE, sputtering and evaporation are currently the main deposition techniques for making superlattices. Electrodeposition also offers advantages however, including cheapness, a high deposition rate and the simplicity of the apparatus. So far most of the research on electrodeposited multilayers has concentrated on metallic multilayers in which magnetic metal layers are sandwiched between two non-magnetic layers, because they exhibit interesting magnetic properties as well as interesting mechanical properties.

Much attention has been paid to metallic superlattices consisting of alternating layers of a ferromagnetic metal e.g.: Ni, Co, Fe or their alloys and a non-magnetic transition or noble metal e.g.: Cu, Ag, Pt, Au and Ru since they can exhibit special properties such as the magneto-optic Kerr effect (MOKE), anisotropic magnetoresistance or giant magnetoresistance [4, 5, 6, 7, 8]. While GMR in Ni/Cu or Ni-Cu/Cu multilayers is small (only a few percent, and hardly reaches 5%), in Co/Cu or Co-Cu/Cu multilayers the effect could be considerably larger. By adding Co ions to the Ni-Cu electrolyte and electrodepositing of Ni-Co-Cu/Cu superlattices, a GMR magnitude of 25% at room temperature was achieved by Nabiyouni et al. [9]. However; the sensitivity of multilayer Ni/Cu films in low magnetic fields (up to 100 Oe) is much larger than that for Co/Cu films.

In the single bath electrodeposition technique, a multilayer is formed by periodically varying either the deposition voltage (potentiostatic control) or deposition current (galvanostatic control) between two suitable values. All of the metal ions to be deposited are present in the single electrolyte used. At a less negative potential the more noble metal present in the solution (say metal A) is deposited on the working electrode, forming layer A, while at a more negative potential (depending on the equilibrium potentials of the metal ions present in the solution) the other metal (say metal B) is deposited and layer B formed. Thus it is possible to electrodeposit metallic superlattices by switching the potential between two suitable values. It should be noted that the more noble metal will be deposited as well as the less noble metal at the more negative potential, so that the real composition of layer B is
AₓB₁₋ₓ instead of B and the superlattice structure will be consisting of alternative layers of A, AₓB₁₋ₓ, A, AₓB₁₋ₓ. Although it is not possible to deposit a layer of pure metal B, the concentration of metal A in the AₓB₁₋ₓ layer may be kept low if the concentration of metal A in the solution is sufficiently low. Fig. 2 shows a schematic diagram for a multilayer structure.

Fig. 2. A schematic diagram for a superlattice structure.

In 1993, it was shown for the first time that electrodeposited short-period metal/metal multilayers consisting of a magnetic layer alternating with a non-magnetic one can exhibit giant magnetoresistance. Since during the MR measurements a constant current passes through the film plane this kind of GMR is called current-in-plane giant magnetoresistance (CIP-GMR) [10]. We measured CIP-GMR values of up to ~25% at room temperature for electrodeposited Cu/Co-Ni-Cu superlattices with Cu layers as thin as ~7 Å and a Co:Ni ratio of 3:1 [11]. For these multilayers, the less noble metal “A” was the Co-Ni alloy, while the more noble metal “B” was Cu.

3. Electrodeposition of Metallic Thin Films onto Semiconductor Substrates

A problem that may have limited the utilization of electrodeposition in modern devices is the requirement that the substrate be conducting which in most cases means metallic. Metals are not, however, the generally preferred substrate for thin film growth due to their physical and electrical properties. Physically they are soft which makes it very difficult to prepare a high-quality defect-free flat surface for deposition, while if the electronic transport properties of the film are of interest these will be short-circuited by the low resistance of the substrate.

A semiconducting substrate has the advantage of allowing resistivity measurements to be made without having to remove the film, as the semiconductor has a much higher resistivity than the metal as well as being partly isolated from the film by the Schottky barrier formed at the semiconductor/metal interface. Semiconductors can also be prepared with flatter surfaces than metals and results achieved would be directly comparable to those for vacuum techniques which also tend to employ semiconducting substrates.

The choice for choosing a semiconductor as the substrate is usually between GaAs and Si, both of which can be readily obtained as high quality polished wafers as they are commonly used in the electronics industry. Si has the advantage of lower cost but the insulating SiO₂ layer should be removed from the surface before deposition. GaAs also has native oxides but these are easier to remove and it had been used in many studies of metal electrodeposition on semiconductors. It is also a commonly used substrate in vacuum deposition of multilayers.

The requirement that the substrate must conduct does not preclude intrinsic semiconductors. By using doped semiconductors it is possible to pass enough current through the bulk of the material to allow electrodeposition, although the mechanisms for charge...
transfer at the solid/electrolyte interface are different between semiconductors and metals. This is especially the case for p-type materials where illumination is often required to generate enough minority carrier electrons at the surface to reduce the ions in solution.

4. Experimental

4.1. Substrate preparation

The as-received (100)-oriented n-type Si wafers from the manufacturer have been chemically and mechanically polished to give a flat mirrored surface. Nevertheless, the surface preparation is required before plating in order to remove dust, grease, impurities and the native oxides that have grown. The wafers resistivity is 1-10 Ω-cm. The Si wafers were cleaved to 20×4 mm rectangular shapes, using a diamond cutter or an appropriate laser beam. Electrical ohmic contact to each substrate was achieved through a GaIn back contact. It can simply be done by painting the back side of Si substrate by GaIn. An adhesive tape was used to mask off all the substrate except for the area on which deposition was desired. The deposition area is a rectangular strip (20×4mm). In order to clean the substrate, the Si wafer surface was first put in the following solutions successively: (i) acetone with ultrasonic vibration for removing the dust and organic substance, (ii) a mixture solution of H₂SO₄ and H₂O₂ for getting rid of grease and impurities, and (iii) 5% HF solution the native silicon oxide. The Si substrate then was rinsed in deionized water, dried by N₂ gas flow and then immediately transferred to the electrodeposition cell.

4.2. Film growth

Our films were grown from a sulfate electrolyte in a three-electrode cell, containing either (Co⁺² and Cu⁺²) or (Ni⁺² and Cu⁺²) ions, for growing Co/Cu or Ni/Cu multilayers respectively. The composition of the electrolytes is given in Table 1. The electrolyte pH was kept constant at 2.0.

<table>
<thead>
<tr>
<th>Co/Cu multilayer</th>
<th>Ni/Cu multilayer</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoSO₄·6H₂O</td>
<td>NiSO₄·7H₂O</td>
</tr>
<tr>
<td>CuSO₄·5H₂O</td>
<td>CuSO₄·5H₂O</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>H₂BO₃</td>
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</table>

We used a procedure similar to that described in our previous paper [3]. When a low negative potential is applied to the substrate, only Cu (the more noble of the metals in the electrolyte) will be deposited, while at higher negative potential Co or Ni will be deposited to form a ferromagnetic layer. Cu is co-deposited with Co or Ni as an impurity in the layer, but Cu concentration in the deposit is kept relatively low by having a low Cu⁺² concentration in the electrolyte. Our multilayered films were grown by alternating the substrate potential between -0.2 and -1.6V relative to a saturated calomel reference electrode approximately 2 cm from the substrate. The computer control potentiostat reads the Co (or Ni) and Cu deposition current signals and sends the data to a computer which is able to plot a graph of the current as a function of time. Fig. 3 shows the variation of current as a function of time for a first few layers of a multilayer consisting of 60[Co(3 nm)/Cu(1.5 nm)]. As the figure shows, while the Cu deposition time (for each Cu layer with a thickness of 1.5 nm) is about a few seconds, the Co deposition time for a 3 nm thick Co layer is about a few microseconds. The reason for that
is that the Co concentration in the electrolyte is much higher than the electrolyte Cu concentration.

![Deposition Current vs. Deposition Time](image)

**Fig. 3.** Deposition current as a function of deposition time for a multilayer consisting of 60 [Co(3 nm)/Cu(1.5 nm)].

The nominal thickness (calculated from the charge passed during growth assuming bulk densities and 100% current efficiency) of Co (or Ni) layers was chosen to be 3 nm and for the Cu layer it was varied between 1 to 5 nm. After electrodeposition the film was removed from the electrolyte, washed with distilled water and then dried with N₂ gas flow.

In order to study the surface morphology of electrodeposited Co/Cu multilayer a selective sample was chosen to be under scanning electron microscopy (SEM) performance. The obtained image is presented in Fig. 4. It can clearly be seen that the film deposition process has been taking place continuously, and the average Co grain size is in the nano-scale.

![SEM Image](image)

**Fig. 4.** SEM image of a Co/Cu multilayer surface.

### 4.3. Magnetic and Electric Measurements

A vibrating sample magnetometer (VSM) was used to study the magnetic properties of electrodeposited superlattices and to plot graphs of the magnetic moment as a function of the applied magnetic field. Two types of sample holder are available, one in which the sample is mounted horizontally and vibrated vertically so that in-plane moment measurements are made, and one in which the sample is mounted vertically either parallel or perpendicular to the magnetic field and vibrated vertically so that both in-plane and perpendicular
measurements can be carried out. All of the VSM measurements were done at room temperature. Figs 5a and 5b show hysteresis loops for Co/Cu and Ni/Cu multilayer films electrodeposited on a Si substrate. The samples consist of 60 bilayers of [Co or Ni (3 nm)/Cu (1.5 nm)]. The Figs clearly show that magnetization of the Ni/Cu multilayer sample saturates in a lower magnetic field than that for the Co/Cu multilayer sample. However the main difference between the two hysteresis loops is the large difference between their coercive fields. The result leads us to introduce the Ni/Cu multilayer as the magnetic sensor in low magnetic fields, while the Co/Cu multilayers are suitable as a magnetic sensor in moderate and high magnetic fields.

![Magnetic Moment vs Magnetic Field](image1)

Fig. 5. Magnetic moment $n$ as a function of magnetic field for a [Co(3 nm)/Cu(1.5 nm)] multilayer a) and [Ni(3 nm)/Cu(1.5 nm)] multilayer b). The multilayers consist of 60 bilayers.

The resistivity measurement equipment consists of a four-point probe assembly and a current source. The four-point probe assembly consists of spring-mounted probes and a voltage-current source. The potential is measured with a micro-voltmeter.

Four-point connections at equal interval distances were made on the sample spring-mounted probes. To check whether all the four connections are conducting electricity or not, I–V studies have been carried out for each sample before measuring the resistivity. Between two points, current was applied and the corresponding voltage drop was measured at different current values. In the same way all the four connections were checked.

![Four Probe Geometry](image2)

Fig. 6. Four probe geometry for thin film electric resistivity.
4.3.1. Four probe method for measuring electrical resistivity of thin films

In this method, four probes are linearly placed on the sample as illustrated in Fig. 6. Current is passed through the outer probes and voltage is measured in between the inner probes. The thin-film resistivity is defined as the ratio of the measured voltage to the applied current.

Since the sample was of a specific geometry with finite thickness, a correction factor C has to be used and the resistivity is given by the following formula:

$$\rho_s = \frac{V}{I} C \left( \frac{d}{a}, \frac{a}{s} \right),$$  \hspace{1cm} (1)

where C is the correction factor which depends on the ratios of $\frac{d}{a}$ and $\frac{a}{s}$. A calculation for thin resistivity is given in reference [12]. Correction factor values for different geometries are given in Table 2.

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<td>-</td>
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<td>4.5324</td>
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</tr>
</tbody>
</table>

5. Magnetoresistance measurements

In order to investigate the variation of the film resistivity as a function of applied magnetic field and study the magnetoresistance effect, the Co/Cu multilayer resistivities were measured as follows: a constant DC current (5mA) is passed through the outer probes and voltage is measured between the inner probes. The ratio of voltage to current gives a quantity which is directly proportional to the film resistivity as described in Eq. 4. The Co/Cu films were then placed in a magnetic field supplied by a DC electromagnet. The applied magnetic field (which is varied between ±2000 Oe) is parallel to the film surface. The giant magnetoresistance (GMR) is defined as [13]:

$$\text{GMR\%} = \frac{\rho(H) - \rho(H_{\text{max}})}{\rho(H_{\text{max}})} \times 100,$$  \hspace{1cm} (2)

where $\rho$ is what we call the film resistivity, and H is the applied magnetic field intensity.

Longitudinal magnetoresistance (LM) is obtained when the magnetic field is applied parallel to the electric current, and in the case of applying the magnetic field perpendicularly to the electric current, a transverse magnetoresistance (TM) is measured. In this work we have grown a series of Co/Cu and Ni/Cu multilayer films. The Co or Ni thickness in each bilayer has been kept constant at 3 nm, while the Cu thickness was varied between 1 and 4 nm. We have obtained a maximum GMR value of 12% for a multilayer film consisting of 60 of Co(3 nm)/Cu(1.5 nm) bilayers. However, the maximum change in resistivity for Ni/Cu multilayers was only 3.5 percent. The result is presented in Fig. 7.
We define the “sensitivity” as the percentage change in the multilayer electric resistivity per unit of applied magnetic field. It can be clearly seen from Fig. 7, while the percentage change in electric resistivity for a Co/Cu multilayer is much higher than that for a Ni/Cu multilayer, the sensitivity of the Ni/Cu multilayer, especially in low magnetic field (up to 100 Oe), is almost twice that obtained for the Co/Cu multilayers. A comparison between Figs 5 and 7 suggest that no strong correlation between MR(H) and GMR(H) is observed in the electrodeposited Co/Cu and Ni/Cu multilayers. This might be due to a weak anti-ferromagnetic coupling between two successive ferromagnetic layers, which leads to a smaller GMR value in the electrodeposited multilayers compared with those grown using physical and vacuum-based techniques. Despite this fact, electrodeposition of multilayer thin films still enjoys the advantages which are mentioned in Section 1.

6. Magnetic sensors based on GMR materials; discussion and conclusion

Resistivity of metals is caused by scattering of conduction electrons. The amount of scattering and hence the resistivity is related to whether the scattered electrons are spin moment up (majority spin) or spin moment down (minority spin) i.e. whether their spin moments are parallel or anti-parallel to the magnetization. Electric current is carried by both spin moment up and spin moment down electrons which may be considered as moving in two different channels with different resistivities. The total current is therefore the sum of the currents carried by spin moment up and spin moment down electrons. In non-magnetic metals, the two currents and hence the resistivities of the two channels are equal, but in ferromagnetic metals and magnetic multilayers they are different.

Giant magnetoresistance arises from spin-dependent scattering with electrons of one spin moment scattered more strongly than those of the other. The fact that for the ferromagnetic transition metals the spin moment down electrons (minority spins) are usually scattered more strongly than the spin moment up electrons (majority spins), can be understood in term of the density of states at the Fermi level [14]. In non-magnetic metals and in the absence of an external magnetic field, the densities of states for spin moment up and spin moment down electrons are equal. Application of a magnetic field splits the spin moment up and spin moment down bands. In ferromagnetic metals, however, the spin moment up and spin moment down bands are split due to the local magnetization, and the result is an asymmetry between the scattering of majority and minority spin conduction electrons. The spin moment down electrons have more unoccupied states available to be scattered into, than the spin...
moment up electrons, and hence they are scattered more strongly than the spin moment up electrons [15]. The resistivity of a magnetic multilayer for each conduction channel (spin moment up or spin moment down) depends on the relative alignment of the magnetizations of neighboring layers. If the magnetizations of successive magnetic layers are anti-parallel, each spin moment direction is alternately strongly scattered when the spin moment direction and the magnetization are anti-parallel, and weakly scattered when the spin moment direction and the magnetization are parallel. The effective resistivity of two successive ferromagnetic layers in an anti-parallel configuration is quite large. If the magnetizations of successive layers in the multilayer specimen are parallel (due to application of a magnetic field), spin moment up electrons are hardly scattered whereas spin moment down electrons are very strongly scattered. Thus the effective resistivity of successive layers in a parallel alignment is quite small.

In magnetic multilayers, if the magnetizations of the magnetic layers are initially anti-parallel to each other, application of an external magnetic field can rearrange them to be parallel to the field and decreases the resistivity of the sample. Since the electric resistivity of multilayer thin films (which is easy to measure) is proportional to the applied magnetic field, one can find the magnitude of the magnetic field by measuring the resistivity of Co/Cu or Ni/Cu multilayers when they are subjected to a magnetic field.

In summary we have successfully grown Co/Cu and Ni/Cu multilayer on n-type Si substrate, using the electrodeposition technique. These multilayers exhibit the GMR property. A maximum 12% GMR was found for Co/Cu multilayers, while the maximum GMR obtained for Ni/Cu multilayers was about 3.5%. However the sensitivity of Ni/Cu multilayers, especially in low magnetic fields (up to 100 Oe) is much higher than that for Co/Cu multilayers. We designed and fabricated Co/Cu multilayers as magnetic sensors for moderate and high magnetic fields, and Ni/Cu multilayers as magnetic sensors for low magnetic fields.

References


