PhD theses booklet

Magnetoresistance Study of Electrolytic Nanostructures

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1. Introduction

Mankind has been using nanotechnology probably since the invention of Damascus steel, although in the ancient times the atomic-range processes leading to better physical properties were surely only the result of the lucky choice of the processing methods. However, nowadays we have the possibitity to develop nanostructures for a desired aim. For example, the atomic range perturbation of the layer thicknessess in metallic multilayers, used in computater industry or in the controlling technology, are able to fundamentally change the phyisical properties of those multilayers.

Magnetoresistance (*MR*) is the change of the electrical resistance due to an external magnetic field. Experimentally, it can be determined from the resistance measured in zero and in H external magnetic fields:

$$MR(H) = \frac{\Delta\rho}{\rho_0} = \frac{\rho(H) - \rho(0)}{\rho(0)} = \frac{\Delta R(H)}{R(0)} = \frac{R(H) - R(0)}{R(0)} \qquad (1)$$

Longitudinal magnetoresistance (*LMR*) is the electrical resistivity mesured when the measuring current is parallel to the external magnetic field and transverse magnetoresistance (*TMR*) is measured when the test current is perpendicular to the external magnetic field.

In 1988, Peter Grünberg and Albert Fert independently investigated the magnetoresistance of Fe/Cr multilayers and sandwich structures prepared by MBE (Molecular Beam Epitaxy). The thicknesses of the individual layers was in the range of the characteristic length of electron transport. The group of Grünberg measured ≈1.5 % change in the resistivity at room temperature, which was by an order of magnitude higher than the magnetoresistance of a 25 nm thick Fe layer. The group of Fert found a 50 % change in the magnetoresistance of [Fe (3 nm) / Cr (0,9 nm)] x 60 multilayers as measured at 4.2 K. The least forseeable aspect of their result was, however, that not only the TMR but also the LMR was negative; i.e., independently from the direction of the magnetization, the resistivity decreased with incresing magnetic field. This newly discovered phenomena was named giant magnetoresistance (GMR) because of the change in the resistivity greater than measured ever before.

2. Aims

The structure of a multilayer strongly influences the GMR measured on the multilayer and the superparamagnetic (SPM) behaviour of the GMR. Therefore, it was decided to investigate how the metals, deposited from an electrolyte, nucleate on a substrate. Great interest was put on the start of the deposition when it is not yet dominated by the previously deposited material but by the substrate. In my case, the well-studied Co/Cu multilayer system was used for this purpose not only because they were easy to prepare but also because of the large *GMR* achievable for this system. My goal was to get known how the GMR changes in the cicumsctances when only a few (even only one) magnetic layers or magnetic–non-magnetic bilyers are deposited on the substrate. Since the measuring system was capable to precisely measure *GMR* even when its value was very small, information could be obtained about the nucleation and the early stage of layer growth through the measurement of the *GMR*. The earlier results of our group was also extensively exploited for this analysis.

Another type of multilayer studied in my work was the Ni-Co/Cu system. This system usually shows a sufficiently large GMR and a low saturation field, which makes their field sensitivity high enough for industrial applications. Though numerous publications are available for this system, only a few of them was carried out under optimal electrochemical cicumstances. Therefore, the first task was to optimize the deposition conditions. Only after this could the GMR be optimized for the largest value through changing the thickness of the individual layers. Additionally, the change in the surface roughness was examined throughout the deposition and also the effect of the changing surface roughness on the GMR properties as the multilayer thickness was changing.

Because in this multilayer system the magnetic layer is an alloy, it seemed reasonable to investigate the magnetic and electric transport properties of these kind of alloys also in bulk form.

Since bulk Fe-Co alloys have good soft magnetic properties, multilayers with this kind of alloy as the magnetic layer can have favorable magnetic properties. Nonetheless, electrodeposited Fe-Co/Cu multilayers have sparsely been investigated, only one paper was published on its GMR properties. This is mainly due to the fact their electrolyitic deposition is very hard becasuse solutions containing Fe^{2+} ions are unstable. Therefore, electrodeposition itself had to be solved as a non-trivial problem for different Fe^{2+}/Co^{2+} ionic ratios. Furthermore, the optimal deposition circumstances had to be found and the optimization for the maximal *GMR* achievable was also an aim of mine.

3. Methods applied

All multilayers and bulk layers were prepared by electrodeposition. The individual layers of the multilayer samples were deposited by pulses applied in the framework of the so-called G/P mode. In this method, the magnetic layer was deposited with a high-current galvanostatic (G) pulse. The Cu content of the magnetic layer could be kept at the level of about 1 % due to the high current density and the large ion concentration ratio in the solution. This low Cu concentration does not cause a measurable effect in the properties of the multilayers. The Cu layer was deposited with a potentiostatic (P) pulse. The potential was optimized for all electrolytes to avoid the codeposition of any magnetic material with copper and also to prevent the previously deposited magnetic layer from dissolving back into the electrolyte.

Magnetoresistance was measured in an electromagnet, able to produce magnetic field up to 8 kOe (0.8 T). The sample with lateral dimensions of 8 mm x 20 mm was put in the 4-cm-wide air gap between the iron cores of 20 cm diameter by using a rotatable sample holder. The normal of the sample plane was perpendicular to the magnetic field and the measuring current was flowing in the sample plane.

The low-temperature measurements were carried out down to 13 K in closed-circuit He cryostat manufactured by LakeShore Cryotronics. The surface roughness was measured with a Veeco Digital Instruments CP-II atomic force microscope (AFM) by scanning a 50 μm x 50 μm area. From the height values obtained, the root-mean-square roughness (R_q) was calculated by the the data processing software of the AFM. Apart from these measuements, the surface roughness was also measured with a ZYGO-LOT NewView 7100-type white light interferometer, having a vertical resolution lover than 1 nm. The scanned area was 0,94 x 0,70 mm^2, the whole vertical scanning range was 65 μm.

The composition was determined for all samples in a JEOL-840 scanning electron microscope (SEM) with an analysing head manufactured by RÖNTEC. The X-ray diffractograms were measured with a Philips X'pert Θ-2Θ type powder diffractometer at the Department of Materials Physics, Loránd Eötvös University.

The thickness of the bulk Ni-Co alloys were measured in the SNMS/SIMS Laboratory of the Institute for Nuclear Research of th Hungarian Academy of Sciences in Debrecen. The instrument was an Ambios Technology prfilometer, having 1 nm vertical resolution.

4. Theses

1. For Ni-Co/Cu and Fe-Co/Cu multilayers, the electrochemically optimal copper deposition potential ($E_{Cu,EC}$) was determined for the first time. At this potential value, neither the dissolution of the previously deposited magnetic layer back into the electrolyte nor the codeposition of any magnetic material with the Cu layer is possible. For Fe-Co/Cu multilayers, the dependence of this potential value on the concentration of Fe^{2+} ions in the electrolyte was found. By using this potential value, the actual layer thicknesses coincides with the previously set values and therefore the dependence of the GMR on the thicknesses of the individual layer thicknesses could be systematically investigated for the first time [*S5*-*S6*].

2. Investigating the GMR characteristics of ferromagnetic/non-magentic multilayers prepared with electrochemically optimal Cu deposition potential as a function of the copper layer thickness, a single maximum in the GMR was only found as a function of d_{Cu}. This Cu layer thickness value does not correspond to the ones measured for multilayers prepared by physical deposition and showing oscillatory GMR, and the shape of the peak is also different.
   a) For Co/Cu multilayers the dependence of the room-temperature resistivity on the copper layer thickness was measured and a maximum was found at $d_{Cu} = 1$ nm nominal thickness [S1]. This Cu thickness coincides well with the d_{Cu} value at which the GMR-AMR transition occurs and thus it suggests that the typical distance of the discontinuities of the copper layer falls into the length scale of the electron mean free path.
   b) For Ni-Co/Cu multilayers, the highest achievable GMR_{FM} value with the lowest possible GMR_{SPM} contribution was determined as a function of the magnetic layer thickness, the non-magnetic layer thickness and the total multilayer thickness. *[S5]*.
   c) For Fe-Co/Cu multilayers, a maximum was found in the value of the GMR as a function of the non-magnetic layer but the thickness of the magnetick layer showed no effect on the magnetoresistance *[S6]*.

3. It was shown for electrolytic Ni-Co bulk alloys that
   a) the residual resistivity, determined by extrapolating the temperature dependence of the resistivity measured between 13 and 300 K to 0 K shows a maximum at the concentration about $Ni_{50}Co_{50}$, i.e. it follows Nordheim's rule, in accordace with experimental values measued on bulk Ni-Co alloys prepared metallurgically [S2].
   b) The *AMR*-values show a maximum at the concentration about $Ni_{70}Co_{30}$ both at 13 K and room-temperature. The 13 K-value of the *AMR* is four times higher than the room-temperature value, in accordace with the experimental values measued on bulk Ni-Co alloys prepared metallurgically [S2].

4. Several series of $Ni_{50}Co_{50}$/Cu multilayers prepared with the optimal Cu deposition potential were produced in order to study the effect of the Cu layer thickness and the total multilayer thickness on the surface roughness as well as on the GMR.
   a) The surface roughness was found to increase exponentially with the increase of the total thickness in the thickness range Σd = 50 – 700 nm. The thicker the Cu layer, the exponential roughening is more dynamic *[S5]*.
   b) A maximum in the *GMR* value was found as a function of the total thickness: the increase of Σd initially makes the *GMR* higher through the increase of the number of the magentic-non-magnetic interfaces but above about 300 nm total thickness the multilayer structure deteriorates, making the *GMR* decrease. *[S5]*.

5. The nucleation properties of ultrathin electrodeposited Co/Cu multilayers containing only a few bilayers were investigated through the measurement of their GMR for the first time [S3].
   a) A linear increase of the surface roughness of the multilayers was found in the thickness range examined.
   b) The exchange reaction, taking place between the atoms of the last deposited Co layer and the Cu^{2+} ions in the electrolyte, makes the surface roughness to decrease. This decrease shows an exponential decay as a function of the time.
   c) Because of the island-like growth of Co and because of the spin-dependent scattering between these island, GMR was found in a Co/Cu bilayer containing only one ferromagnetic layer. The Cu, deposited between the Co islands, acted as a separating „layer".

d) A linear increase of the GMR_{SPM} contribution with the increase of the surface roughness was observed through the experimental determination of the GMR_{SPM} contribution as a function of the total multilayer thickness and the surface roughness as a function of the total multilayer thickness.

6. The change of the surface roughness of $Ni_{50}Co_{50}$/Cu multilayers was studied as a function of the E_{Cu} copper deposition potential used [S4].
   a) It was found that for potentials more negative than the electrochemically optimal $E_{Cu,EC}$ value where both Ni and Co codeposits with Cu, the surface roughness drastically increases and the multilayer structure deteriorates. In contrast, for potentials more positive than $E_{Cu,EC}$, the roughness decreases because of the dissolution of the magnetic material (mainly of the Co in the magnetic layer). For NiCo/Cu multilayers deposited at more negative potentials than $E_{Cu,EC}$, a much higher surface rouhness was measured than for the multilayers deposited at the same potentials but containing only Co or only Ni as the magnetic layer. The surface roughness as a function of the Ni:Co ratio in the magnetic layer shows a maximum at the 1:1 concentration ratio. Therefore, the reason of the increase in the surface roughness has to be looked for in the anomalous codeposition of Ni and Co. Perhaps the adsorbed reacion intermediates present on the surface during the deposition affects the deposition of Cu by deteriorating the lateral homogenity.
   b) In the magnetoresistance as a function of the Cu deposition potential, a maximum was found at a potential more positive than the optimal Cu deposition potential. This is a result of two competing effects. The smoothening of the magnetic layers, coming from the dissolution of the magnetic material, makes the GMR higher. However, because of the dissolution, the magnetic layer becomes thinner and thus the Cu layer becomes thicker, which decreases the measured GMR by reducing the number of the magnetic-non-magentic transitions per unit length. These two effects result in the observed position of the GMR-maximum, different from the electrochemically optimal $E_{Cu,EC}$ value.
   c) It was shown that the value of the GMR_{FM} contribution correlates well with the evolution of the surface roughness: the GMR was the highest for the smoothest multilayers. For the multilayers with low surface roughness, the improvement of the multilayer structure was also observable by the appearance of satellite peaks on the X-ray diffractograms.

5. Conclusions

During the experimental research presented in the thesis, the structural changes of electrodeposited multilayers was investigated both in the early phase of the deposition and at large total multilayer thicknesses. Because electrodeposition is a non-equilibrium preparation method, special attention had to be payed on the resulting structural changes, which, according to my results, play a crucial role in the magnetic properties of the prepared nanostructures. In addition, the electrolyte is a reactive environment; therefore, its reactions have to be taken into account when preparing nanostructured materials. A reaction, for example the exchange reaction, can also be advantageous (higher GMR because of the smoother layers) and also disadvantageous (the magnetic layer can partly dissolve and thus form islands, the actual layer thicknesses are not known) effects on the physical property for which optimization has to be done. This depends on if the preparation conditions were sufficiently controlled or not.

6. Publications

[S1] I. Bakonyi, E. Simon, B. G. Tóth, L. Péter and L. F. Kiss: Giant magnetoresistance in electrodeposited Co-Cu/Cu multilayers: Origin of absence of oscillatory behaviour, *Physical Review B* **79**, 174421/1-13 (2009) {IF = 3,475; FH = 10}[1]

[S2] B.G. Tóth, L. Péter, Á. Révész, J. Pádár, and I. Bakonyi: Temperature dependence of the electrical resistivity and the anisotropic magnetoresistance (AMR) of electrodeposited Ni-Co alloys, *Eur. Phys. J. B* **75**, 167-177 (2010) {IF = 1,575; FH = 9}

[S3] B.G. Tóth, L. Péter and I. Bakonyi: Magnetoresistance and Surface Roughness Study of the Initial Growth of Electrodeposited Co/Cu Multilayers, *J. Electrochem. Soc.* **158** (11), D671-D680 (2011) {IF = 2,590; FH = 1}

[S4] B.G. Tóth, L. Péter, J. Dégi, Á. Révész, G. Molnár and I. Bakonyi: Influence of Cu deposition potential on the giant magnetoresistance and surface roughness of electrodeposited Ni-Co/Cu multilayers, *Electrochim. Acta* **91**, 122-129 (2013) {IF = 3,832*}

[S5] B.G. Tóth, L. Péter, J. Dégi and I. Bakonyi: Magnetoresistance and surface roughness study of electrodeposited $Ni_{50}Co_{50}$/Cu multilayers (manuscript before submission)

[S6] B.G. Tóth, L. Péter and I. Bakonyi: Preparation and Magnetoresistance Study of Electrodeposited Fe-Co/Cu Multilayers (manuscript in preparation)

[1] IF: impact factor, FH: number of independent citations
* 2011 value