

# Electrodeposition and investigation of metallic nanostructures

- Ph.D. thesis booklet -

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2013

# 1. Introduction

Nowadays, nanotechnology is gaining more and more importance. The preparation and investigation of nanostructured materials are very important tasks of science. Namely, the investigation of these materials has revealed, that many of the physico-chemical processes take place in a different way in nanostructured materials than in macroscopic (bulk) materials. The explosive emergence of nanotechnology has opened new horizons in science.

The date of first mention of nanotechnology is exactly known: on the 29<sup>th</sup> of December 1959, the Nobel prize-winner scientist Richard Feynman gave a lecture at the annual meeting of the American Physical Society held at the California Institute of Technology. The title of the lecture was: „There's Plenty of Room at the Bottom”. This lecture about the problem of controlling material preparation on a very small scale predicted that one day science would be able to help writing the entire contents of an encyclopedia on the head of a pin. Extrapolating the known laws of physics, he imagined a technology that would follow the basic process of nature, the construction of nano-objects atom by atom, molecule by molecule. The first scientific publication on this topic was born in September 1981. Since that time, several studies published about the production of nano-objects have confirmed this prediction and nowadays it is already possible to build up desired nanostructured materials at the atomic level based on preliminary assessment.

The nanotechnology has made unknown areas of use available, and the properties of the nanotechnology-treated surfaces have gone through a revolutionary change. Such properties include light transmission, scratch and abrasion resistance, electrical conductivity and resistance to corrosion. With these new materials, a number of everyday-used products were produced, such as rain- and dirt-repelling clothing, moisture-resistant sunscreen, bandages antibiotic properties.

For me, one of the most important area of nanotechnology is nanoscale electrodeposition.

The structural, magnetic and electrical transport properties of magnetic/non-magnetic multilayers have been investigated for two decades in the former Metals Research Department (Complex Fluids Department since January 2013) of Wigner Research Centre of HAS. Various metals and metallic alloys with a number of unique properties have already been prepared by electrodeposition (e.g., amorphous Ni-P alloys, nanocrystalline nickel and cobalt as well as magnetic/nonmagnetic multilayers such as Ni-Cu/Cu, Co-Cu/Cu, Co-Ni-Cu/Cu).

The thickness of the electrodeposited layers of the multilayers can be controlled in the nanometer range, and the nominal layer thickness agrees well with the results of direct structural measurement. This indicates that sample preparation can be controlled fairly precisely even on the nanoscale, thus it is possible to investigate the physical properties of these materials as a function of the preparation parameters. The investigations by Fert and Grünberg in 1988 led to the observation of

the phenomenon of the giant magnetoresistance (GMR) effect in magnetic/non-magnetic multilayers and this discovery was awarded with the Nobel Prize in Physics in 2007. Thus, the investigation of magnetoresistance properties is very important for this group of materials.

The analysis of the near-substrate zone of metallic nanostructures can provide useful information about the electrodeposition process itself and about the depth profile of the deposit. In addition, we can get more information about the near-substrate zone of alloy deposits and this is important since this zone is formed during a transient (non-stationary) stage of electrodeposition. Our group (Electrodeposited Nanostructures Group) developed a sample preparation technique for depth profile analysis of deposits by which the sample can be separated from the Si wafer substrate and, thus, the starting surface of the sample for the depth profile analysis is sufficiently smooth. So this so-called reverse depth profile analysis can investigate the change of the composition in the near-substrate zone more sensitively as in the case of starting the analysis from the much rougher final deposit surface.

## 2. Aims

My work focused on the electrodeposition and investigation of metallic nanostructures, and on the investigation of the relationship between the preparation parameters, the magnetic properties of the electrodeposited material and the electrochemical behavior. I tried to utilize the widest possible range of available experimental techniques to achieve these goals.

During the plating process, at the very beginning of the deposition, a transient zone is formed until the steady-state conditions of the electrodeposition process are reached. However, this steady state may not be reached in the case of coatings which are thinner than 200 nm. So the composition of the alloy film which forms in the transient zone can change continuously along the thickness and this can affect the properties of the deposit. Therefore, I aimed at investigating the composition of the near-substrate zone of thin electrodeposited Fe-Ni layers and making a comparison of d.c.-plated and pulse-plated samples.

In the case of the Ni-X (X = Cu, Cd, Sn) systems, my aim was to investigate the preferential deposition phenomenon of other metals preferentially depositing with Ni and to see if the change experienced in the composition distribution for the Fe-Ni system (i.e., the relative accumulation of the preferentially depositing component near the substrate) can be generalized for these systems.

In the case of the Co-Cu system, magnetic/non-magnetic Co/Cu multilayers were electrodeposited by choosing an appropriate bath composition. In the case of Co/Cu multilayers made by physical methods, for the prevention of the island-like growth of the Cu layer, so-called surfactant metallic additives (e.g., Pb or Bi) are used. My aim was to study whether this works

also for electrodeposition, and to study the effect of Pb, Bi as well as Ag as additive components on the magnetoresistance of the deposit. In the case of bismuth-containing baths, I was also interested in the investigation of the electrodeposition in strongly acidic media because this media is favorable for the solubility of Bi(III) salts.

The electrodeposition of Co/Cu multilayers was already carried out from several baths and at various temperatures in the past, but the effect of the deposition temperature has not yet been investigated systematically. Therefore, in the case of electrodeposited Co/Cu multilayers, my aim was to investigate how the deposition temperature effects on the magnetoresistance of the deposit.

In the case of the Co-Ni/Cu system, my aim was to study the magnetoresistance and the structure of samples prepared from modulated composition baths at different temperature, because this has not yet been studied systematically formerly.

My another aim was to develop baths which are appropriate for the codeposition of lead and cobalt to prepare continuous films, alloys and multilayers in this system.

### **3. Methods applied**

#### ***3.1. Sample preparation by electrodeposition***

All multilayers and bulk layers were prepared by electrodeposition (direct-current and pulse plating).

The substrate was a metal-coated 0.26 nm thick Si wafer with (100) orientation. A 5 nm thick Cr adhesive layer was followed by a 20 nm thick Cu conductive layer (both layers were produced by evaporation). Atomic force microscope measurements indicated that the roughness of these substrates was at most 3 nm.

Electrodeposition was carried out by using an *ELEKTROFLEX EF453* type potentiostat-galvanostat. During electrodeposition, a two- or three-electrode cell was used. During sample preparation, the Si/Cr/Cu wafer was the cathode (the working electrode), but in some studies, the cathode was a more noble metal (Cu or Pt) than the metal to be electrodeposited. The cross section of the cell was rectangular but at the bottom of the cell, the cross-section area was smaller close to the cathode. The anode (the counter electrode) was immersed in the solution at the open upper end of the cell. The counter electrode was always the metal with the higher deposition potential, and some studies were made by an inert electrode (e.g., Pt). For the measurement of the potential of the cathode (galvanostatic mode) and the setting of the potential of the cathode (potentiostatic mode and CV measurements), a saturated calomel electrode (Hg(l)|Hg<sub>2</sub>Cl<sub>2</sub>(s)|KCl(sat)) was used. The reference electrode was in contact with the cell through

a Luggin-capillary to reduce the ohmic potential and to help the reproducibility of the reference electrode position.

For experiments on the investigation of the effect of bath temperature, another cell layout was used. There was some difference between the two cells as follows: for the latter cell, the cross section was circular and the top of the cell was closed for ensuring a more homogenous temperature distribution. The anode was combined with the top of the cell.

### ***3.2. Sample preparation for reverse depth profile analysis***

In the case of reverse depth profile analysis for Fe-Ni and Ni-X (X = Cu, Cd, Sn) alloys, after the electrodeposition of the Fe-Ni and Ni-X alloy, a Ni cover layer was also electrodeposited on top of the sample as a mechanical support. After breaking the Si wafer, the deposit remained intact. The thickness of the Ni cover layer was 2  $\mu\text{m}$ .

### ***3.3. Analytical methods***

The chemical analysis of the composition of the electrodeposited samples was made by JEOL JSM 840 type scanning electron microscope with a RÖNTEC analytical probe. The chemical analysis was carried out over a 1 mm<sup>2</sup> area of the sample, typically at 3 points, with 25 kV voltage.

The electrochemical quartz crystal microbalance (EQCM) measurements were performed by aSRS-200 instrument by using a gold-plated quartz crystal. The base frequency of the crystal was 5 MHz.

The depth profile analysis was carried out by an SNMS instrument in the SNMS/SIMS Laboratory of the Institute for Nuclear Research of the Hungarian Academy of Sciences in Debrecen. The instrument was an INA-X type (SPECS GmbH, Berlin) SNMS apparatus. The diameter of the ion-bombarded circular area was 2-3 nm which was defined by a Ta mask. The energy of the Ar<sup>+</sup> ions was 350 keV during the sputtering. This ion energy is an order of magnitude smaller than what is typically used for removing the surface layers, e.g., in the case of XPS. This energy is low enough so the sample does not cause any significant miscibility during sputtering.

The deposit thickness necessary for calculating depth profile analysis was also measured in Debrecen in the same laboratory, the instrument was an Ambios Technology profilometer having 1 nm vertical resolution.

### ***3.4. Physical methods***

The magnetoresistance was measured in an electromagnet able to produce magnetic fields 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 measuring current was flowing in the sample plane and the magnetic field was oriented along the sample plane. The magnetoresistance measurements were performed in a sample holder with a four-point-contact probe. For each sample, the magnetoresistance was measured both in longitudinal (LMR) and transverse (TMR) configurations. In the longitudinal configuration, the direction of the magnetic field and the current are parallel, in the transverse configuration, they are perpendicular to each other.

The X-ray diffractograms were measured with a Philips X'pert  $\Theta$ - $2\Theta$  type powder diffractometer at the Department of Materials Physics, Eötvös University.

## 4. Theses

### A) Results of d. c. and pulsed deposition on Fe-Ni samples with SNMS reverse depth profile analysis for testing [S3]

- T1. It was established by the results of depth profile analysis of d.c.-plated and pulse-plated samples that the component distribution in the two kinds of deposits is substantially different. In the case of pulse-plated samples, there is only a small difference in the steady-state and the initial composition. It is possible to prepare homogenous samples by this method. By contrast, in the case of d.c. electrodeposition, there is a drastic difference between the two values, so those samples have variable composition in the direction of growth.
- T2. It was proved that in the case of pulse-plated Fe-Ni samples, the initial composition is independent of the current density when the current density used for the sample preparation is between -12 and -30 mAcm<sup>-2</sup>. The initial composition of d.c. electrodeposited samples is the same as the average composition of pulse-plated samples prepared with the same current density pulse amplitude as used during pulse plating.
- T3. In the case of pulse plating, the larger is the duty cycle, the higher is the change in the composition compared with the initial composition. If the Fe<sup>2+</sup> concentration is 45 mmol dm<sup>-3</sup>, a duty cycle  $\varepsilon < 0.2$  is necessary for constant alloy composition along the whole thickness whereas in the case of 5 mmol dm<sup>-3</sup> Fe<sup>2+</sup> concentration, this can only be achieved for a duty cycle  $\varepsilon < 0.04$ . For pulse plating, the smaller the Fe<sup>2+</sup> content of the bath, the lower duty cycle should be chosen in order to ensure that the composition of the deposit does not change along the thickness. In the case of d.c. electrodeposition, when the duty cycle is 1, the deposit reaches steady-state composition after 90 nm but the molar fraction of the Fe will be only the half of the initial value.

**B) Results on electrodeposited Ni-X (X = Cu, Cd, Sn) alloys investigated by SNMS reverse depth profile analysis [S1]**

- T4. It was proved for several Ni alloys that, in the case of d.c. electrodeposition, the preferentially depositing metal (Cu, Cd, Sn) enriches in the near-substrate zone which is 150 nm thick, thus for thinner alloy coatings it is not possible to ensure a homogeneous composition profile of the electrodeposited material by d.c.-plating.
- T5. In the case of Ni-Sn alloys, it was proved that the substrate atoms (Cu) migrate into the electrodeposited layer. The mixing of the substrate atoms with the electrodeposited alloy is caused by the strong alloy-formation tendency of Cu and Sn.

**C) Results on the investigation of the influence of bath temperature in the case of Co/Cu and Co-Ni/Cu multilayers**

- T6. In the case of electrodeposited multilayers, the effect of the temperature of the bath used on the magnetoresistance of the electrodeposit was investigated systematically for the first time. While in the case of Co/Cu multilayers an effect of bath temperature on the magnetoresistance properties of the deposit was observed, for Co-Ni/Cu multilayers it was not possible to establish such a trend from the results of the magnetoresistance measurements. In the case of Co/Cu multilayers, the increase of the temperature increased the ferromagnetic contribution to the magnetoresistance.

**D) Results of investigations of the influence metallic additives and anion types in the case of electrodeposited Co/Cu multilayers**

- T7. By analyzing the effect of lead as metallic additive, it was found that increasing the lead cation concentration in the bath, the magnetoresistance decreases monotonically. It was an overall experience in acetate and perchlorate baths experiments that the lead cations have not floating-layer (surfactant) effect on the multilayer formation but these cations have rather a structure-breaking effect. The giant magnetoresistance changes in the presence of these two anions at different rates as a function of the lead cation concentration (with the same nominal film thickness).
- T8. In the case of Co/Cu multilayers which were electrodeposited in perchlorate bath, a positive effect of silver occurs on the magnitude of the GMR effect. The GMR values of Co/Cu multilayers are larger by about a factor 2 in the presence of an optimal  $\text{Ag}^+$  concentration, in comparison with samples electrodeposited in silver ion-free baths under the same experimental conditions.

## E) Results for electrodeposited Co/Pb granular mixtures [S2]

- T9. It was shown that among the investigated baths complying the solubility conditions, Co and Pb codeposition is possible only in acetate bath. It was ascertained, based on cyclic voltammograms, that the deposition and the dissolution potentials of Pb fall between the deposition and dissolution potential of Co, so in the case of pulse-plating, electrodeposition of Pb is not accompanied by the dissolution of Co in the deposition potential range of Pb.
- T10. It was shown that while d.c. deposition does not yield compact deposits below 80 at.% Co content, in the case of pulse plating this is possible at any deposit composition. It was proved by composition analysis that if the deposition potential of lead is in the range  $-0.58\text{ V} - -0.63\text{ V}$  with respect to a saturated calomel electrode, and the deposition current density of the Co-rich material is in the range  $-10 - -50\text{ mAcm}^{-2}$ , then the composition of the sample is determined by only the charge passing through the bath during the pulses.
- T11. The results of several experimental methods clearly show that in the Co-Pb system not exhibiting miscibility under equilibrium conditions, electrodeposition either cannot yield significant miscibility of the two metals and multilayer formation also does not happen by electrodeposition. This conclusion can clearly be inferred from the results of X-ray diffraction measurements, and it is supported by the magnetoresistance measurements as well.

## 5. Conclusion

During my studies, I investigated the depth composition profile of electrodeposited Fe-Ni alloys under several conditions. The pulse plating mode is suitable for the preparation of Ni-Fe alloy deposits with smooth composition profile even for thicknesses below 200 nm. It was found that the lower the ion concentration of the preferentially depositing metal in the solution, the lower the duty cycles required to ensure a homogeneous component distribution.

It was found for all systems investigated that under d.c. electrodeposition conditions the preferentially depositing component is enriched in the near-substrate zone of the deposit. These results on the deposition of metallic alloys underline the importance of monitoring the composition of ultrathin deposits and suggest the use of pulse-plating mode from the practical point of view.

During my studies, I investigated the influence of different ions on electrodeposited Co/Cu multilayers to compare the electrochemical deposition technique with results of physical deposition methods described in the literature. The effect of Pb as metallic additive was structure-breaking rather than smoothing. Contrary to Pb, a positive effect of Ag on the magnitude of the GMR of Co/Cu multilayers was revealed although the nature of the measured  $MR(H)$  curves did



not confirm that the same strongly antiferromagnetically coupled multilayer structure occurred as observed for physical deposition methods.

I investigated in detail the composition, structure and magnetotransport properties of Co-Pb deposits prepared by two-pulse electrodeposition in G/P mode. The samples are not textured in any direction and it is probable that a granular mixture of the two components is created.

## 6. Publications underlying the thesis as well as other publications

### Publications supporting the Ph.D thesis

[S1] K. Neuróhr, A. Csik, K. Vad, A. Bartók, G. Molnár, L. Péter;

Composition depth profile analysis of electrodeposited alloys and metal multilayers: the reverse approach

*Journal of Solid State Electrochemistry* **15** (2011) 2523–2544. [IF(2011): 2,131]

[S2] K. Neuróhr, J. Dégi, L. Pogány, I. Bakonyi, D. Ungvári, K. Vad, J. Hackl, Á. Révész, L. Péter;

Composition, morphology and electrical transport properties of Co-Pb electrodeposits

*Journal of Alloys and Compounds* **545** (2012) 111-121. [IF(2011): 2,289]

[S3] K. Neuróhr, A. Csik, K. Vad, G. Molnár, I. Bakonyi, L. Péter;

Near-substrate composition depth profile of d.c.-plated and pulse-plated Fe-Ni alloys

*Electrochimica Acta* **103** (2013) 179– 187 [IF(2011): 3,832]

### Other publications

[S4] P. Jedlovsky, G. Hantal, K. Neuróhr, S. Picaud, P. N. M. Hoang, P. von Hessberg and J. N. Crowley;

Adsorption Isotherm of Formic Acid on the Surface of Ice, as Seen from Experiments and Grand Canonical Monte Carlo Simulation

*Journal of Physical Chemistry C* **112**(24) (2008) 8976-8987. (IF: 3.396; FH = 3)

[S5] K. Zih-Perényi, K. Neuróhr, G. Nagy, M. Balla, A. Lásztity;

Selective extraction of traffic-related antimony compounds for speciation analysis by graphite furnace atomic absorption spectrometry

*Spectrochimica Acta Part B* **65** (2010) 847-851. (IF: 3.549; FH = 2)

[S6] M. Jafari Fesharaki, L. Péter, T. Schucknecht, D. Rafaja, J. Dégi, L. Pogány, K. Neuróhr, É. Széles, G. Nabyouni, I. Bakonyi;

Magnetoresistance and structural study of electrodeposited Ni-Cu/Cu multilayers.

*Journal of the Electrochemical Society* **159**(3) (2012) D162-D171. (IF: 5)