

Electrodeposition of Cu/CoNi(Cu) GMR Superlattices

P. L. Cavallotti, R. Vallauri, A. Vincenzo
Dip. Chimica Fisica Applicata – Politecnico di Milano
Via Mancinelli,7 – 20131 Milano, Italy

Cu/CoNi(Cu) GMR superlattices were electrodeposited from a single sulfamate electrolyte containing Rochelle salt, at pH 6.4, by a triple current pulse deposition technique.

The influence of three different substrates, namely Si/NiFe20%, Si/ITO (indium tin oxide) and Si/Cr, on the crystalline structure, the bath electrokinetic behavior and the GMR effect were examined.

The electrokinetic behavior was characterized with square current pulses superimposed during layer growth. Structure and surface morphology were characterized by X-ray diffraction and Scanning Electron Microscopy.

The relations between the growth properties of Cu/CoNi(Cu) superlattices and the electrokinetic behavior during deposition are pointed out and discussed with reference to the observed multilayers GMR effects.

For more information, contact:

P. L. Cavallotti

Dip. Chimica Fisica Applicata – Politecnico di Milano

Via Mancinelli,7 - 20131 Milano, Italy

Phone: +39-02-23993149

FAX: +39-02-23993180

E-mail: pietro.cavallotti@polimi.it

Introduction

Giant Magnetoresistance (GMR) in magnetic metal films was first reported for the Fe/Cr¹ system and since then has been the subject of many investigations. The peculiar physical properties of metal/metal superlattices and their application as magnetic field sensors make the GMR effect a topic of considerable interest for both fundamental and technical reasons.

Although the most important methods to obtain GMR films are sputtering and molecular beam epitaxy, also Electrochemical Deposition (ECD) must be examined with particular attention, as it is possible to produce multilayers or modulated films of suitable composition and thickness by properly adjusting and controlling the operation conditions². ECD processes are intrinsically less expensive than vacuum methods; operation temperature is low in comparison with physical deposition and it is possible to obtain thin films onto substrates of almost any shape. However, the complexity of the electrochemical effects, occurring during metal/metal superlattice deposition, deserves further investigation in order to improve the film microstructure and functionality.

This paper deals with the GMR effect in ECD CoNi(Cu)/Cu multilayers. The microstructure and electrokinetic behavior during multilayers growth on different substrates were studied in order to find possible correlation between electrochemical and structural data. The results of this investigation are related to the observed GMR effects, reported in a previous work³; the importance of electrochemical factors, determining particular micro-structural features, is stressed.

Experimental

Multilayers electrodeposition was carried out from a single electrolyte⁴⁻⁶ containing cobalt, nickel and copper sulfamates and Rochelle salt (NaKC₄H₄O₆). Plating baths were prepared from chemicals of analytical grade and double distilled water and treated with active charcoal. Table 1 gives baths composition and plating conditions. The copper concentration in the electrolyte was adjusted in order to minimize the copper content in the electroplated magnetic layers. Solutions were de-aerated by nitrogen bubbling before plating. Deposition was carried out under gentle stirring; the temperature was maintained at 48°C.

A triple current pulse technique was utilized⁷. A cycle consisted of a long (4÷60s) low current pulse (copper deposition step); a short (1÷3s) high current pulse, during which cobalt and nickel are mainly deposited; a short (0.1s) off time pulse to help the potential relaxation between high and low current pulse.

An AMEL System 5000 potentiostat-galvanostat was used for the multilayers deposition.

Table 1: Baths composition and plating conditions

	Bath 1 [mol/l]	Bath 2 [mol/l]
Coσ ₂	0.04	0.05
Niσ ₂	0.02	0.025
Cuσ ₂	0.006	0.005
NaKC ₄ H ₄ O ₆	0.18	0.18
σ = NH ₂ SO ₃ ⁻ pH = 6.40 T = 48°C		

The Cu/CoNi(Cu) multilayers were deposited onto silicon wafers, coated with the following sputtered seed-layers:

- SiO₂(100nm)/Ni₈₀Fe₂₀ (20nm) (substrate B)
- ITO(*Indium Tin Oxide* -160nm) with Au ECD flash (substrate D)
- SiO₂/Cr(70nm) + Au ECD flash (substrate E).

Microstructure, composition and morphology were characterized with X-ray diffraction (XRD), microanalysis by Energy Dispersion Spectroscopy (EDS) and Scanning Electron Microscopy (SEM).

The magnetoresistance ratio was measured with respect to the resistance at the highest applied magnetic field. The saturation magnetoresistance is the highest resistance in the experimental field, normalized with respect to the resistance at the highest magnetic field, defined by $\Delta R/R(\%) = (R(H) - R(H_{max})) / R(H_{max})$. GMR ratio [%], Middle Height Width [Oe], Coercivity [Oe] and Sensitivity [%/kOe] were measured at room temperature with a low-frequency lock-in amplifier using a standard four contacts technique and applying a magnetic field parallel to an AC current flowing through the sample.

No correction was made for substrate contribution.

Results and Discussion

Copper was deposited at 0.5 mA/cm^2 ; the cobalt-nickel alloy at $5\div 6 \text{ mA/cm}^2$, a current density c.d. little less than the CoNi(Cu) limiting c.d., which was about $7\div 9 \text{ mA/cm}^2$. The ferromagnetic layer was characterized by about 20:1 Co to Ni ratio and Cu content less than 30 %at³.

Composition modulated coatings with good crystallinity and well define layered structure were obtained, as shown by the appearance of first order satellite peaks on both sides of fcc (111) and fcc (200) reflections of XRD patterns. Figure 1 shows the XRD pattern of a sample grown on Si/SiO₂/Cr/Au of 8nm deposited modulation length.

Satellite peaks are observed when a super-lattice structure occurs, of higher dimensions with respect to the periodicity of the crystalline lattice. Satellite peaks are observed on both sides of the main crystal lattice diffraction peaks, at diffraction angles (θ^+ , θ^-) according to the relation:

$$\frac{2 \cdot \sin(\theta^\pm)}{I_x} = \frac{1}{d} \pm \frac{n}{\Lambda} \quad [1]$$

where Λ is the superlattice modulation length, n is the satellite peak order, d is the distance between the crystalline planes and λ_x the X-ray wavelength. The measured modulation length, corresponding to the satellite peaks found in the XRD pattern (7.87nm and 8.04 nm respectively) is in good agreement with the expected value (8nm).

A GMR effect increase was observed at Cu layers thickness higher than 3.5 nm. The highest GMR values were found for Cu layer thickness ranging from 5 to 8 nm. Increasing Cu layer thickness, GMR ratio increased, while the ratio of fcc(111)/fcc(200) XRD peak intensity decreased. The same correlation between GMR and copper thickness was observed for multilayers electrodeposited onto different substrates. GMR effect increased with t_{CoNi} and showed a maximum at 3nm. The CoNi(Cu) thickness at which the GMR maximum occurred was unaffected by Cu-layer thickness and substrate. Nominal thickness do not take into account possible change in current efficiency, and the actual CoNi(Cu) layers thickness could be lower than 3nm.

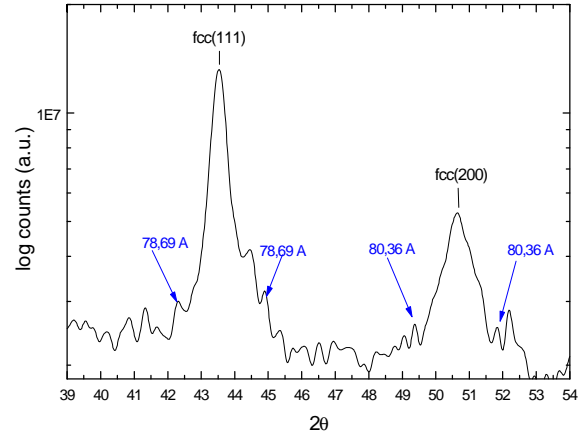


Figure 1: XRD pattern from a [Cu(5nm)/CoNi(Cu)(3nm)]₄₀ multilayer grown onto Si+Cr(20nm)+Au ECD flash.

Substrate influence

Multilayer growth is strongly influenced by the substrate material and its behavior. The most important effects are on the bath electrokinetics or on the deposit structure. The substrate can have a significant impact on nucleation and during early stages of multi-layer growth, influencing nucleation overvoltage or showing electrocatalytic behavior towards the hydrogen discharge reaction. Structure and morphology of the growing film strongly depend on epitaxial effects. In this frame, both the preferred orientation and surface roughness of the substrate show the most important influence. Also the substrate material electrical conductivity is important, determining the extent of the GMR effect, as measured without corrections.

Different substrates were tested in order to investigate the effect of the substrate material and surface roughness on GMR and magnetic properties of multilayers.

Substrate B was a Si wafer with 100nm SiO₂ and 20nm Ni₈₀Fe₂₀ seed layer. The surface was mirror bright with very low roughness, below 0.02 μm . Multilayers electrodeposited onto this substrate show very low coercivity, down to <40 Oe. Substrate D is a Si wafer on which a 160nm film of Indium Oxide doped with Tin (ITO) was deposited. ITO substrates, showing low electrical conductivity, were coated with a gold ECD flash before the multi-layer deposition.

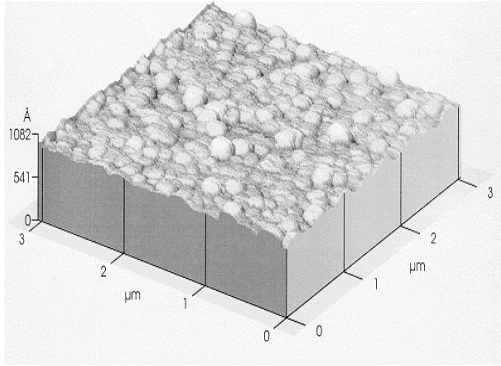


Figure 2: AFM topography of Si/ITO substrate with Au ECD flash.

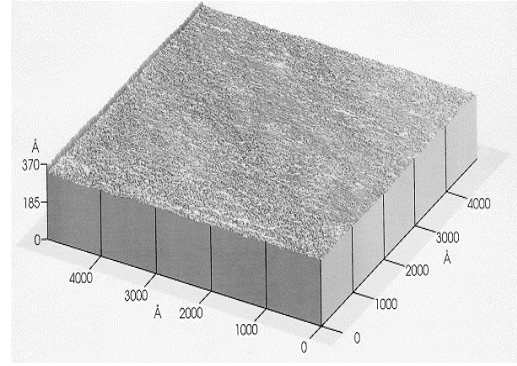


Figure 4: AFM topography of Si/SiO₂/Cr(70nm) substrate with Au ECD flash.

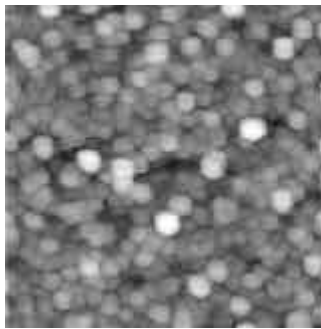


Figure 3: AFM micrograph of Si/ITO substrate with Au ECD flash (3μm x 3μm).



Figure 5: AFM micrograph of Si/SiO₂/Cr(70nm) substrate with Au ECD flash (0.5μm x 0.5μm).

ITO has a cubic Indium Oxide (In₂O₃) crystalline structure with [111] preferred orientation; the surface was of considerable roughness (see Figure 2 and Figure 3). Substrate E is Si/SiO₂/Cr 70nm; also on this substrate a gold ECD flash was deposited in order to permit the multi-layer deposition. Surface was smooth and uniform, as shown in Figure 4 and Figure 5.

According to our results³, the brighter, more uniform and smoother was the substrate, the higher were the sensitivity and the lower were coercivity and Middle Height Width of GMR curves.

Table 2 gives the comparison between GMR measurements of different multilayers grown on substrates B, D and E respectively.

As shown by the SEM micrograph in Figure 6, taken on a [Cu(7.5nm)/CoNi(Cu)(3nm)]₄₀ sample, multilayers grown onto substrate D showed large grain size, in the range of 250 nm. Both substrate and deposit displayed a coarse surface. ΔR/RMAX% values up to 6.90% were obtained, a consequence also of the substrate low conductivity; sensitivity was about 40%/kOe.

Table 2: GMR measurements of multilayers grown onto different substrates.

ML Structure	Substrate	Bath	GMR [%]	Sensitivity [%/kOe]	Coercivity [Oe]	MHW [Oe]
[Cu(5nm)/CoNi(Cu)(3nm)] ₄₀	B	1	5.0	45.9	45	155
[Cu(5nm)/CoNi(Cu)(3nm)] ₄₀	D	2	6.9	48.8	150	200
[Cu(5nm)/CoNi(Cu)(3nm)] ₄₀	E	2	5.4	41.1	110	175

Very low surface roughness and fine grain size were obtained on substrate B and E. Figure 7

shows a SEM micrograph from a [Cu(7.5nm)/CoNi(Cu)(3nm)]₄₀ ML deposited onto



Figure 6: SEM micrograph of [Cu(7.5nm)/CoNi(Cu)(3nm)]₄₀ ML grown onto Si+ITO(160nm)/Au ECD flash (substrate D).

substrate E. These substrates favor the formation of well-structured multilayers: with the modulation improvement a high $\Delta R/R_{MAX}\%$ value was observed of about 6.0%, although substrates B and E are more conductive than D, and sensitivity value was up to 55%/kOe.

XRD analysis showed that the degree of [111] texture negatively affects the GMR response of the multilayer²; no other significant differences was observed with regard to the crystal structure of multi-layers grown onto different substrates³. Therefore, besides the epitaxial effect on multilayer growth, the main influence of the substrate is on the interface structure and morphology.

The electrochemical growth of multilayers was characterized by recording the potential profile during deposition. Figure 8 show the potential transients observed for the first two superlattice layers on substrate D and E, and Figure 9 for the following layers on substrates B, D and E. The potential change depends also on the ohmic drop in the electrolyte, but this value is constant, maintaining the relative significance of the data.

A copper nucleation overpotential is observed depositing onto substrate D, whilst it is negligible for substrate B; this occurs unexpectedly, notwithstanding that the first copper layer on substrate D is formed on a gold thin film (see Figure 8). A possible influence of the hydrogen evolution reaction at such low



Figure 7: SEM micrograph of a [Cu(7.5nm)/CoNi(Cu)(3nm)]₄₀ ML grown onto Si/SiO₂/Cr(70nm)/Au ECD flash (substrate E).

potential cannot be neglected, in agreement with the lower overpotential observed for permalloy. During the second deposition cycle, Cu overpotential slightly decreases depositing on substrate D, while it increases on substrate B. CoNi(Cu) alloy deposition shows a higher overpotential for substrate D than for substrate B; during the deposition of the first layers a slight overpotential decrease occurs on substrate D, whilst no perceptible change occurs on substrate B.

The potential transients in steady state condition for multilayer growth are reported in Figure 9. The overpotentials for Cu layer and CoNi(Cu) layer electrodeposition on substrate B (permalloy) remain almost unchanged, with respect to the starting values, whilst the same overpotentials depositing on substrate D are consistently decreased.

The observed behavior suggests two possible consequences: since the potential gap between copper and magnetic alloy deposition is higher for substrate D than for substrates B or E, the resulting layered structure can be defined better for D than for B or E; on the other hand, since the potential of copper deposition is lower for substrate D than for B or E (which represents the intermediate case), it could promote undesired effects such as cobalt oxidation or dissolution. Actually, the latter case can be ruled out, in view of the high electrolyte pH.

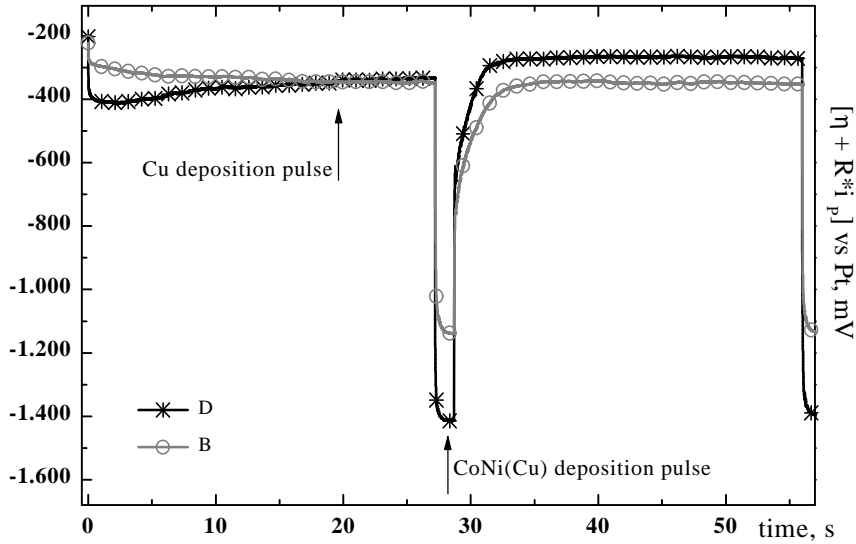


Figure 8: Potential transients for the first two Cu/CoNi(Cu) layers on substrate B [SiO₂/Ni₈₀Fe₂₀ (20nm)] and D [Si/ITO(160nm)/Au ECD flash].

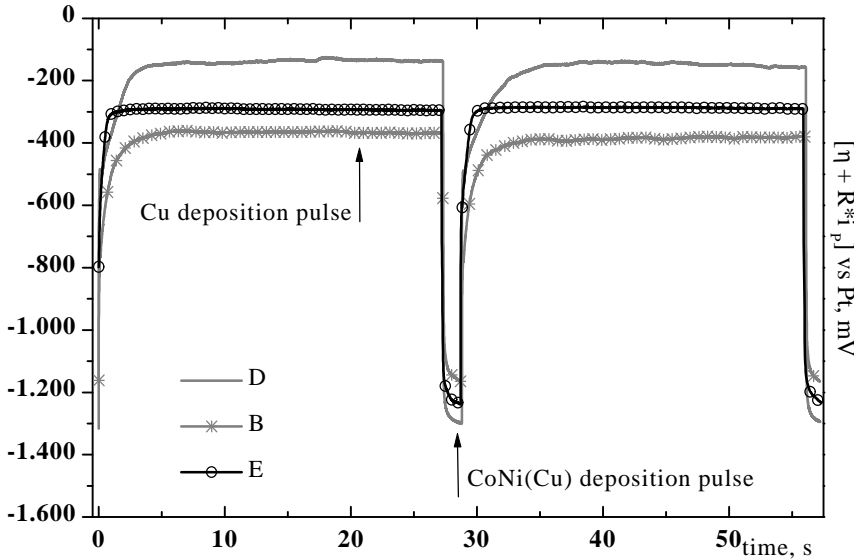


Figure 9: Potential transients for [Cu(5nm)/CoNi(Cu) (3nm)]₄₀ multilayer on substrate B [SiO₂/Ni₈₀Fe₂₀ (20nm)], D [Si/ITO(160nm)/Au ECD flash] and E [Si/SiO₂/Cr(70nm)/Au ECD flash].

The electrokinetic behavior of the bath during layer deposition was characterized with the Secondary Current Pulse (SCP) technique. The SCP method was previously described^{8,9}. Short square current pulses, of duration from 4 to 6 ms and c.d. i_p ranging from $2 \cdot i_D$ to $6 \cdot i_D$ mA/cm² (with i_D deposition c.d.), are overimposed during deposition at i_D . A modified version of the SCP model was used in this work, to account for slightly raising overvoltage during the current pulse perturbation. The overvoltage transient is described with a two terms equation: the first resulting from the equivalent circuit of the potentiometric cell (consisting of the parallel of a non-linear resistor with Tafel characteristic and a variable adsorption capacitance); the second from

a linearized Sand-type contribution. The following equation of the overpotential transient results:

$$h(t) = B_T \cdot \ln \left[\frac{i_p}{i_D} - \frac{i_p - i_D}{i_D} \cdot \exp \left(- \frac{i_D \cdot t}{B_T \cdot C_{ads}} \right) \right] + \frac{RT}{zF} \cdot \sqrt{\frac{t}{\tau}} \quad [2]$$

with parameters: B_T [mV/decade] the transient Tafel slope, C_{ads} [μ F/cm²] the adsorption pseudo-capacitance, τ [ms] the relaxation time; while i_D is the deposition c.d. and i_p the pulse c.d.

B_T is related to the asymptotic value reached after charging; if a steady state is not reached at the end of the pulse, when phenomena preceding or parallel to the charge transfer step appear to influence the cathodic process, B_T can be inferred

from the time behavior of the transient. The capacitance behavior at the electrodic surface is related to the nature and amount of electroactive species adsorbed at the electrode and the law $C_{ads} \cdot \exp(\eta/B_i) \cdot (d\eta/dt)$ is assumed, taking into account the influence of the surface overpotential η also on the capacitance change at the electrodic surface. A linear relationship between $\tau^{1/2}$ and $1/i_p$ was observed, while the product of $\tau^{1/2}$ times i_p was not constant, thus showing that the observed phenomena do not conform to the case of electrode reaction controlled only by diffusion¹⁰.

The SCP technique was applied to the study of the CoNi(Cu) layer deposition, since the explorative work carried out during Cu layer deposition showed that the electrode reaction is to a large extent under diffusion control: the transient overpotential increases roughly linearly with the square root of time.

Electrochemical measurements were performed in a three-electrode configuration, with a Platinum/Titanium reference electrode, at pH 6.40, T 48°C and gentle stirring. Ohmic drop due to solution resistance, η_ω , could be readily inferred from the shape of the transients and a linear relationship between η_ω and $(i_p - i_D)$ was found to hold in all instances.

Transient recording experiments were carried out according to the following scheme. The first transient was recorded while imposing a 11 mA/cm² – 4ms cd pulse on the sample just after the *first* CoNi(Cu) deposition step (6 mA/cm² – 1.5s).

The other transients were recorded at the end of step 6 in the following sequence:

1. Cu deposition c.d. pulse: 0.5 mA/cm² – 27s;
2. CoNi(Cu) deposition c.d. pulse: 6 mA/cm² – 1.5 s;
3. Off-time pulse: 0 mA/cm² – 0.1 s;
4. Step 1;
5. Step 2;
6. cd pulse: i_p mA/cm² (i_p was set at different values: 11, 16, 26, 31 mA/cm²) – 4 ms;
7. Step 2.

The experiments were performed on the three different substrates:

- B) Si/Ni₈₀Fe₂₀(20nm);
- D) Si/ITO(160nm) with Au ECD flash;
- E) Si/SiO₂/Cr(70nm) with Au ECD flash.

The SCP parameters for CoNi(Cu) layer deposition onto the different substrates are listed in Table 3.

Table 3: Transient parameters for CoNi(Cu) layer deposition onto three different substrates.

Substrate	$B_T (1^{st})^*$ (mV/dec)	B_T (mV/dec)	$C_{ads} (1^{st})^*$ ($\mu F/cm^2$)	C_{ads} ($\mu F/cm^2$)	$\tau^{1/2}$ (ms)
B	131	180	96	47	-2.224+90.35/ i_p
D	180	176	25	53	-0.169+14.84/ i_p
E	162	170	65	40	-1.773+77.05/ i_p

Contrary to Cu layer deposition, CoNi(Cu) layer deposition is predominantly under activation control.

The observed electrokinetic behavior may be summarized as follows: the electrodic pseudo-capacitance is low, in the range 40 ÷ 60 $\mu F/cm^2$; B_T is high, in the range 3RT/F; this value can be considered exempt from concentration polarization contribution and dependent on the peculiar character of the crystallization reactions at the growing electrode.

Such high values are observed in steady state conditions only in case of diffusion related

phenomena or slow chemical reaction, such as dissociation of complexes, preceding the electron transfer step and playing a relevant role in determining the reaction rate. B_T values in the range of 3RT/F were already observed by us¹¹ in conditions giving cluster growth.

Tafel slope values, observed in the same c.d. electrodeposition range from potentiodynamic curves are close to 2RT/F.

* 1st is referred to the first CoNi(Cu) deposition step.

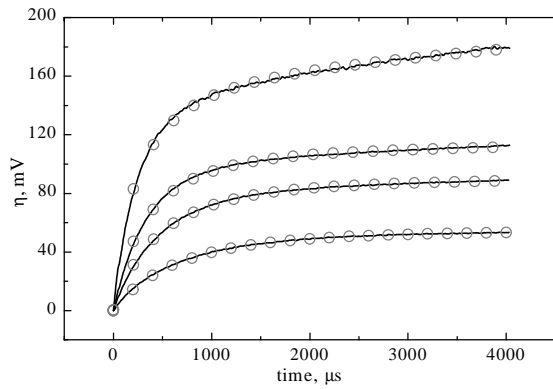


Figure 10: Transient overvoltage (full line) and SCP interpretation (circles) for CoNi(Cu) deposition on substrate B; pulse c.d.: 11, 16, 26, 31 mA/cm².

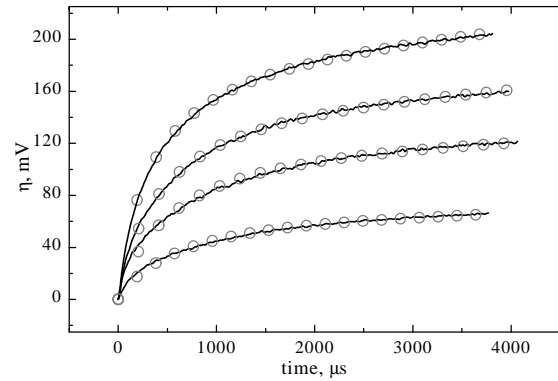


Figure 12: Transient overvoltage (full line) and SCP interpretation (circles) for CoNi(Cu) deposition on substrate D; pulse c.d.: 11, 16, 26, 31 mA/cm².

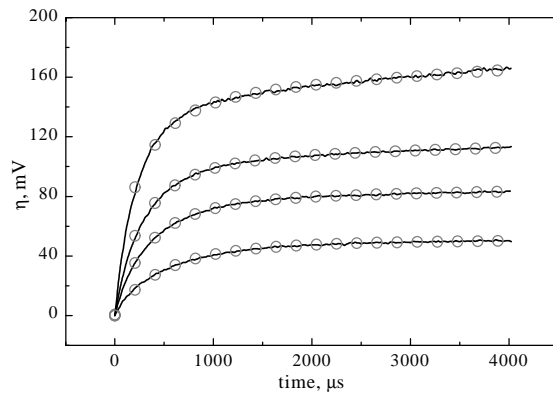


Figure 11: Transient overvoltage (full line) and SCP interpretation (circles) for CoNi(Cu) deposition on substrate E; pulse c.d.: 11, 16, 26, 31 mA/cm².

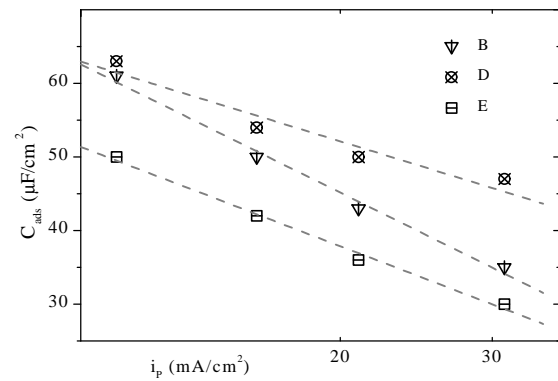


Figure 13: Electrode pseudo-capacitance vs pulse current density for the different substrates.

In the case of Si/Ni₈₀Fe₂₀ substrate, a B_T value of about 130 mV/dec, with a corresponding high value of pseudo-capacitance, was observed during the first CoNi(Cu) deposition step, that is during the growth of the first cobalt alloy layer on the first copper layer grown directly onto the NiFe substrate. This value, around $2RT/F$, can be related to the hydrogen discharge reaction and suggests that hydrogen may strongly affect the early stages of ML growth onto NiFe substrate. In the further steps of growth onto NiFe substrate, the estimated B_T values agree well with the general behavior observed. The extremely low initial C_{ads} value in the case of Si/ITO substrate can be attributed to a partial surface coverage, as well as to the semiconductive behavior of the substrate. The pseudo-capacitance C_{ads} values

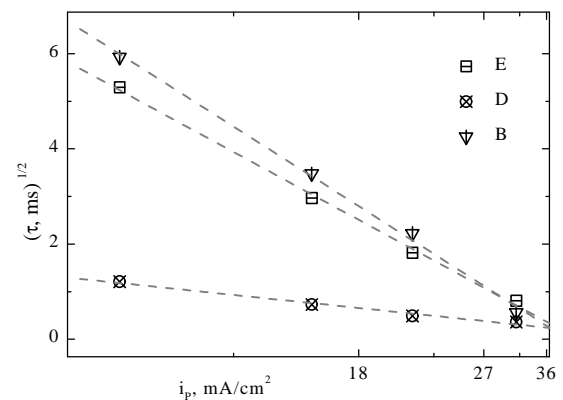


Figure 14: $\tau^{1/2}$ vs the reciprocal of the pulse current density for the different substrates.

seem to be influenced by c.d. more than by the surface state at the growing electrode: a logarithmic relationship between C_{ads} and the pulse

c.d. is found (see Figure 13).

Low values of the relaxation time τ were necessary to fit the experimental transients: square root of τ shows a linear relationship with the reciprocal of the pulse c.d. (see Figure 14). τ values were also found to depend on stirring, showing a limited reproducibility.

Conclusions

1. Surface type influences the electrokinetic behavior of the electrolyte during multilayer growth; this can be mainly attributed to the different substrate roughness.
2. GMR properties of the electrodeposited ML were in part a direct consequence of surface roughness (the smoother the surfaces, the lower coercivity and MWH), in part possibly influenced by the electrolyte behavior (maximum GMR effect and sensitivity for ITO substrate).
3. The proposed solution permits a good sublayers definition, being in a range of pH where surface etching is minimized during periods without current.
4. SCP technique gives transients that are accurately interpreted with a simple model; measured parameters are related to the cathodic discharge mechanism:
 - transient Tafel slope B_T value is $3RT/F$, typical of cluster growth;
 - pseudo-capacitance C_{ads} mainly depends on the real surface, i.e. on the roughness;
 - relaxation time τ depends on substrate and on pulse c.d.: it is mainly related to a reaction step involving intermediate adsorbed species, playing a definite role in the discharge reaction.

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