Magnetic anisotropy of nickel nano-coatings deposited by cathodic voltammetry

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ABSTRACT

Nanocrystallized Ni coatings of thickness values ranged from 70 nm till about 1.20 µm and grown by cathodic voltammetry (C-V) technique are investigated varying the scan rate (*r*) of the related (C-V) curves in the interval $0.167 \le r \le 1.67$ mV/s. Thinner coatings obtained at higher *r* values have rougher surfaces while lower *r* values leads to thicker and smoother samples. Their magnetic reversal is ruled by the domain wall (*DW*) nucleation and motion. Ferromagnetic and topography characteristics of the samples reveal the existence of a common critical thickness $d_c \approx 375$ nm for both their microstructure and magnetic nano-structures. The magnetic anisotropy of Ni samples exhibit a predominant parallel component for the thinnest samples while the perpendicular one grows with the thickness increase.

1. INTRODUCTION

A ferromagnetic film under an applied magnetic field exhibits a magnetic anisotropy that reflects its global energetic feature including several contributions as the magnetostatic, magnetocrystalline, magnetoelastic term s and so on [1, 2]. Its reactivity proceeds from local structures consisted of magnetic domains (*MD*) and domain walls (*DW*) that could exhibit various configurations. In fact, anisotropy and magnetic structure are both closely linked as widely reported. Maze-like domain patterns of $La_{0.7}Sr_{0.3}MnO_3$ films for instance have been associated with perpendicular magnetic anisotropy [3]. Similarly, the weak dense stripe domains of Fe₇₈ Si₁₀ B₁₂ films were found as the origin of out-of-plane anisotropy [4]. The study of this inter-dependence revealed that the material quantity or film thickness should be taken into account [5-7]. Regarding nano-sized thick films, the deviation of their characteristics from those of bulky materials still remains an important investigation area for which the role of the film deposition technique and related applied conditions are essential. They directly affect the feature of the film-substrate interface region and the film surface irregularities or topography [2-7]. The last aspect can no longer be ignored nowadays as nano-structured and nano-crystallized films are being currently

used in many application fields [8-11]. The reported observations on this topic mostly result from investigation of specific magnetic materials^{2,10}. Theoretical analyses supporting these observations are somehow scarce and those existing are expected to obey particular conditions. In that case, the straightforward treatment proposed by Zhao et al [9] seems worthwhile to be tested with different materials obtained from various experimental protocols. By and large, such a study mostly concerns ultra-thin films made of some monolayers (ML) or samples having thickness values confined below some hundreds nanometers. They are usually prepared in high vacuum systems from costly physical methods as ion implantation, sputtering and metal evaporation [12,13]. A technologically cheaper procedure as electrodeposition has numerous acting parameters that can be explored for improving the film guality. Nano-crystallized nickel coatings investigated in the present work are deposited this way on gold substrate using cathodic voltammetry technique as widely described elsewhere[14]. Dependence of their ferromagnetism on microstructure aspects induced by the deposition scan rate (r) is here examined from sample thickness values of some tens nano-meters till about one micron. It is shown that the magnetic anisotropy and domain structures have here a common specific critical film thickness. Its position is shifted at higher values compared with the results commonly found.

2. EXPERIMENTAL

Ni coatings are prepared in a three-electrode cell system from a 1M Ni (SO₄)₂ aqueous electrolyte (pH=3.5) made of a FLUKA products. The working electrode or stationary substrate of 0.5 cm² area is made of an evaporated gold film of [111] preferred orientation. grown in a face-centred cubic (fcc) structure on chrome-coated glass slide. A platinum plate of the same area forms the counter electrode while a saturated calomel one (SCE) serves for the potential reference. The electrochemical experiments are performed with a radiometer PGP 201 potentiostat from which nickel films are obtained by cathodic voltammetry, the related (C-V) curves being drawn at different scan rates (r) ranged in the interval 0.167 $\leq r \leq 1.67$ mV/s commonly considered as low speeds [14]. The film thickness is measured from a commercial STRATAGem (SAMx France) software associated with xray microanalysis, the related spectra being acquired at about 25 kV in a collecting time of 100 s, as described in Ref [15,16]. Once formed, the Ni coatings structure are analysed from a BRUCKER D8 ADVANCED x-ray apparatus with a Cu(K α) irradiation λ =1.540 Å. Their global magnetic properties are examined at room temperature with a vibrating sample magnetometer (VSM) of LAKE SHORE COMPANY. The samples topography and magnetic images are directly obtained from a scanning probe microscope (SPM) Nanoscope IIIa (VEECO) operating in AFM/MFM dual mode. Magnetic CoCr-coated tips of approximately 17 nm apex radius with a cantilever of 0.06 N m⁻¹ spring coefficients are used here with a resonance frequency of about 70 kHz. The domain structure investigation is carried out from MFM analysis performed in the tapping/lift mode, which allows the collection of both the topography and magnetic-force images of the same sample surface area. The oscillating magnetic cantilever shift is measured at a constant tip-top (tip-sample) distance of about 100 nm and a spatial resolution of 10 nm. In all cases, the tip is initially magnetized with a field perpendicular to the sample plane, no external magnetic field being applied during the Ni sample analysis.

3. RESULTS AND DISCUSSION

According to the deposition method used, the scan rate is the main acting parameter of the film's growth process and hence the one of the induced film microstructure including the surface morphology and thickness. In the present section, these particular aspects of the Ni electrodeposits are analysed first as they can provide some interesting indications for the study of their global and

local magnetic characteristics.



Fig. 1 - 3D AFM images of nanocrystallized Ni coatings obtained at the two extreme scan rates: (a) at r = 1.67 mV/s ; (b) at r = 0.17 mV/s

3. 1 Microstructure and topography evolution of Ni coatings

Recently, we showed that Ni coatings formed on Au substrate by the method described here grow through an epitaxial process regardless of the r value, leading to the faced centred cubic (fcc) phase of [111] preferred orientation [14]. The AFM images proposed in Fig.1 denote that although their global grain size is affected by the deposition scan rate, their vertical hemi-ellipsoïd shape remains similar as it appears for the two extreme investigated r values. It appears here that the grain size regularly increases with r while ddecreases. This thickness behaviour is likely to be explained by a higher stabilization of Ni ad-atoms at lower r values due to a better charge transfer equilibrium at the film-substrate interface. Besides, the increase of r possibly engenders a modification in the film's growth process confirmed by the marked grain size change and the rapid decrease of d value observed at higher scan rates.

Scan rate r (mV/s)	Film thickness d (nm)	Surface roughness σ (nm)	Lattice parameter <i>a</i> (Å)	Strain ε (%)
0.17	1142	86	3.4736	- 1.43
0.33	379	94	3.4780	- 1.31
0.88	251	100	3.4817	- 1.20
1.67	76	120	3.5097	- 0.41

Table 1 - Topography and strain dependences on scan rate of Ni coatings

The results in Table I show that the lattice mismatch between Ni and Au leads to a compressive stress effect during the film formation regardless of *r* value. Actually, the lattice parameter of the Ni samples deduced from x-ray analysis always remains lower than $a_0 = 3.5241$ Å of bulk. One observes that the bigger grains of thinner films are less stressed than the smaller ones of thicker samples. The topography modification of the Ni films due to scan rate is investigated using the Family-Viscek method widely described in our previous works [14,18]. The measured saturated root-mean-square surface roughness (σ) of the coatings increases with *r*. The study of roughness-thickness dependence reveals the strong surface perturbation of Ni coatings at the smallest thickness range, the smoothness increasing with *d* value. This result is quite opposite to those of most reports for which the increase of film thickness leads to the one of grain size and surface roughness [6,19]. In any case, it appears here that the interdependence of *d* and σ should be taken into account in the magnetic behaviour of the investigated Ni nano-coatings.

3. 2 Magnetic characteristics of the investigated Ni coatings

a) - Hysteresis loop and global magnetic feature of Ni samples

Normal $M(H_{\perp})$ and parallel $M(H_{\parallel})$ magnetization of the investigated Ni samples were invetsigated in the applied magnetic field region -10 < H < +10 KOe. The results proposed in Fig 2(a) related to 1 µm-thick film show that the magnetization mode engenders different hysteresis loops having specific saturation thresholds. In actual fact, one sees that $M(H_{\perp})$

saturates at nearly $(H_s)_{\perp}$ =7.50 KOe while $M(H_{\ell})$ reaches the asymptotic point at $(H_s)_{\ell}$ =1.02 KOe. This implies that normal field requires more energy to saturate the material than parallel one due to a large demagnetization field along that direction. A similar result has been observed with all our investigated samples. That confirms the fact that varying the scan rate in the film deposition process as done here keeps a certain common feature in the global material magnetic anisotropy.

Although the configuration of hysteresis loops is similar, the film thickness is expected to modify the material magnetic characteristics. For that purpose, the study is undertaken in a more narrow applied field $(H_{l/l})$ interval -2 < H < +2 KOe. Fig. 2(b) reports the results of the two extreme film thickness values d = 76 and 1142 nm for which the hysteresis loop of the thinnest sample is slightly more rectangular. The study of their respective squareness $S=(M_{r/l}M_s)$ defined as the ratio of the remanence (M_r) on the saturation magnetisation (M_s) in Fig.3(a) denotes relatively close values while the two samples exhibit a quite different coercivity (H_c) in Fig.3(b).



Fig. 2 - Magnetic hysteresis loops: (a) of the 1142 nm thick Ni sample under parallel and normal applied fields; (b) of the two extreme samples under a parallel field

Examination of the remaining investigated samples clearly reveals a non monotonous evolution of H_c and S versus film thickness. The squareness reaches a maximum for a film thickness of about 375 nm while coercivity depicts a minimum at nearly the same d value. It can be observed in Fig 3(a) that Ni coatings exhibit larger squareness values (S > 0.5). This indicates that their magnetic reversal is ruled by the (*DW*) nucleation and motion for which the coercivity proceeds from a delay in that process [10, 24]. Accordingly, the film morphology induced by the deposition scan rate is likely to play an essential role. Actually, the biggest grains of the thinnest samples can be considered as originated by initially isolated nucleation sites from which the vertical growth of the material is mostly favoured. As it appears in Fig.1(a) they can be considered as weakly coalesced, which engendered

a weak magnetic interaction between them. A longer delay in the DW nucleation and motion leading to higher H_c values is expected in that case, as shown in Fig. 3(b). The increase of *d* goes together with a more effective coalescence during the film formation that leads to a better interaction between smaller grains, which evidently favours the DW motion and the lowering of coercivity.

The decreasing trend observed below d = 350-400 nm is consistent with the Néel theoretical prediction expressed as $H_c = A.d^{-n}$ where A and n are the fitting constants [19]. The slight increase of H_c in a full coalescence phenomenon for d values higher than 400 nm implies that the corresponding delay in the *DW* nucleation and motion has another origin.



Fig.3 - Dependence of the global magnetic characteristics of Ni nanocoatings on the sample thickness : (a) Squareness S=(Mr/Ms); (b) Coercivity (H_c)

b) - Local magnetic feature of Ni samples from SPM analysis

In agreement with the results of Fig.1, the 2D-AFM topography images (I) of Fig. 4 mainly depict the grain size difference of the Ni samples. However, they always remain the necessary reference for the study of their local magnetic configuration (II) as the same surface area is concerned. The grain numbering proposed here portrays a better correlation of the results obtained in both analyses at the two extreme *r* values. For the sample related to *r* =1.60 mV/s (*d* = 76 nm), one sees in Fig. 4 I(a) that the granular features numbered 1, 2 in the topography image are quite reproduced in the magnetic phase of Fig. 4II(a). Actually, the bright and dark dots of that MFM image respectively reflect the up (repulsive interaction) and down (attractive interaction) electron spin states. They clearly denote the presence of mono-domain in the material magnetic structure. The smaller grains of the thicker film (*d* =1142 nm) in Fig. 4 I(b) obtained at *r* = 0.17 mV/cm give rise to a maze pattern of Fig. 4II(b) commonly associated with multi-domain magnetic structural

evolution induced by the film deposition scan rate. Usually, such a structural change is only assigned to the film thickness [17,22,23]. Owing to the (r– d) dependence established below, one can admit that both parameters have a role in the results obtained. However, further work remains necessary to evaluate their individual contribution.



Fig. 4 – 2D SPM images of Ni nano-coatings obtained at the two extreme scan rate values: (I) from AFM and (II) from (MFM) for the two film thickness values d = 76 nm (a) and d = 1142 nm (b)

3. 3 Evolution of the magnetic anisotropy in the Ni coatings

The results presented above imply that an evolution of the magnetic anisotropy with the deposition scan rate could be expected. The first indication is given by the hysteresis

loops of Fig. 2(a) for which the parallel magnetization of Ni nano-coatings requires less energy than the perpendicular one. Furthermore on their anisotropy can be deduced from the global approach of a film under an applied magnetic field effect for which the energy per unit volume is expressed as [24]:

$$E = -M * H + 2\pi M^2 \cos\theta + K_1 \sin^2\theta + K_2 \sin^4\theta$$
(1)

where the first term depicts the interaction of the magnetization with the external field (Zeeman effect); the second term accounts for the shape anisotropy energy; the third and fourth terms are the uniaxial magnetic anisotropy with K_1 and K_2 the second and fourth order anisotropy constants. θ is the customary angle linked to the spherical coordinates. According to Ha *et al* [30], K_1 includes the magneto-static, magneto-elastic and surface energy terms while K_2 includes the bulk magneto-crystalline and magneto-elastic ones. The minimization of Eq. (1) leads to the saturation magnetization conditions for which the saturated coercivity is expressed as:

$$\left(H_{s}\right)_{\perp} = -\frac{2K_{leff}}{\left(M_{s}\right)_{\perp}} \tag{2}$$

for perpendicular magnetization, the parallel one leading to the as follow relation :

$$(H_s)_{ll} = \frac{2K_{1eff}}{(M_s)_{ll}} + \frac{4K_2}{(M_s)_{ll}}$$
(3)

where $K_{1eff} = K_1 - 2\pi (M_s)^2$, the effective anisotropy constant, includes both the uniaxial magnetocrystalline and shape contributions. K_{1eff} is directly determined from the experimental $(H_s)_{\perp}$ and $(M_s)_{\perp}$ of the Ni coatings using Eq (3).

The results of Table 2 indicate that K_1 is negative in our thickness range in agreement with reported data for relatively thicker films and the Ni crystal [30]. K_{1eff} also remains negative for the investigated scan rate region, which confirms the uniaxial magnetization of the samples and their in-plane magnetization easy axis regardless of the applied *r* value.

As reported for some other Ni/substrate (Cu, glass, Si) systems [2,5,19,24], the dependence of K_{1eff} on *d* is evident due to the sensitivity of M_s and H_s on *d* illustrated in Fig. 2. However, the relatively higher K_{1eff} values obtained here are likely to be typical of the film growth process as induced by the scan rate and the specific Ni/Au interface properties. The tendency for the magnetisation to be in-plane or out-of-plane is generally quantify from the product ($K_{1eff} \times d$) as proposed in the model of Ha *et al* [2] and the work of Bochi *et al* [29]. The ($K_{1eff} \times d$) versus *d* curve of the investigated Ni samples depicts in Fig. 5 a decreasing profile in the negative region, ($K_{1eff} \times d$) being more negative with the increase of *d*. Referring to the cited models, it can be admitted here that *d* =76 nm of our thinnest Ni sample is already larger than the thickness limit (d)_{*l*} for which the material exhibits positive ($K_{1eff} \times d$) values associated with the perpendicular anisotropy. Actually, (d)_{*l*} << 20 nm are reported for the Ni/Cu (001) and Cu/Ni/Cu systems [2,5,21]. Although (d)_{*l*} can be affected

Scan rate <i>r</i> (mV/s)	<i>K_{1eff}</i> (x10 ⁶ erg.cm⁻³)	<i>K</i> ₁ (x10 ⁶ erg.cm⁻³)	<i>K</i> ₂ (x10 ⁶ erg.cm⁻³)
0. 17	- 1. 56	- 0. 08	0. 98
0. 33	- 1. 78	- 0. 30	1. 05
0. 88	- 1. 94	- 0. 46	1. 15
1.67	- 1. 91	- 0. 43	1. 08

by the film growth conditions, our results obtained from 70 < d < 1150 nm are in a full agreement with the models above.

Table 2 - Deposition scan rate and the magnetic anisotropy constants of the Ni coatings

One deduces that all our Ni coatings have an in-plane magnetization easy axis as it appears in Fig. 2(a). However, if the magnetic anisotropy of the 76 nm-thick Ni sample ($K_{1eff} \times d = 13.50 \text{ erg.cm}^{-2}$) has a predominant in-plane component, the anisotropy of the 1142 nm-thick sample ($K_{1eff} \times d = 180.45 \text{ erg.cm}^{-2}$) is rather more out-of-plane.

This interpretation fully concurs with the maze pattern of that thicker sample in Fig. 4II(b), which reflects the presence of a more marked perpendicular component of the film magnetic anisotropy [12]. The experimental determination of $(H_s)_{//}$ and $(M_s)_{//}$ from the Ni electrodeposits permits the calculation of K_2 using Eq. (4). The results proposed in Table 2 indicate that this constant is always positive regardless of the film deposition scan rate. In connection with K_1 , this result reflects a gradual anisotropy transition in the material between the two extreme directions (parallel and perpendicular) with the film thickness [30]. Plotting the product ($K_2 \times d$) versus d depicts an increasing curve profile. One deduces that the thicker the film the higher is the contribution of the magneto-elastic effect at the film-substrate interface due to the lattice mismatch of the materials involved.

Ausanio *et al* [13] reported that this effect engenders an increasing stress in the material, which corroborates quite well the increase of the structural strain with the Ni film thickness obtained here from x-ray analysis (see Table I). Note that this stress is admitted to be the origin of the perpendicular component of the film magnetic anisotropy leading to stripe or maze patterns, as shown here in Fig 4II(b).



Fig. 5 – Characterization of the effective magnetic anisotropy of Ni nano-coatings

4. CONCLUSION

In general, cathodic-voltammetry method serves to the identification of red-ox species in electrochemical systems. We show here that it can be a successful technique for the deposition of nano-crystallized and nano-structured coatings for which the scan rate parameter plays a determining role in the morphology and topography of the samples obtained. Compared to various substrate materials effects investigated earlier [14], gold substrate offers wider grain size and roughness amplitudes of Ni coatings keeping the same grain shape. The deposition method proposed here gives rise to Ni coatings having a magnetic anisotropy made of parallel and perpendicular components although their magnetization easy axis always remains in-plane. Owing to the change induced by the deposition scan rate to the second and fourth order constants K_1 and K_2 , it seems interesting to examine the canting angle of the magnetic anisotropy and then investigate on the necessary conditions to optimize its perpendicular or out-of-plane component. Work in this direction is currently being carried out in our team.

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