Role of p-Hydroxybenzhydrazide Additive in Electrodeposition of Thin NiP Film Used as a Nonmagnetic Spacer in Laminated (CoFe/NiP) Nano Structures

Steve Riemer, a Ming Sun, b,* and Ibro Tabakovic c,* a
Seagate Technology, Research and Development, Bloomington, Minnesota 55345, USA
bWestern Digital, Fremont, California 94539, USA
cECE Department, University of Minnesota, Minneapolis, Minnesota 55435, USA

Electrodeposition of NiP film used as a thin nanomagnetic spacer in laminated multilayer (2.4T CoFe/NiP) nan-perpendicular writer pole for recording magnetic heads is described. The electrodeposition of laminated multilayers was carried out in a dual-bath automated electroplating tool. The thin NiP films with thickness from 2 to 5 nm were obtained as nonmagnetic amorphous NiP alloys with P-content higher than 18 at.%. The problem of composition gradient at the CoFe/NiP interface was solved by using a p-hydroxybenzhydrazide organic additive in the plating solution. The details of the electrodeposition of NiP films, the role of p-HBHy and properties of electrodeposited NiP films and CoFe/NiP multilayers are discussed.

© The Author(s) 2016. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI:10.1149/2.0461606jes] All rights reserved.

The purpose of this paper is to report a new electrochemical method for fabrication of very thin films with 23–25 at. % P as a nonmagnetic spacer in laminated multilayers (2.4T CoFe/NiP) used in perpendicular writer pole of the recording heads. The use of electrodeposited or sputtered 2.4T CoFe as a material for perpendicular writer pole, with their intrinsically high magnetostriction (50–60 × 10−6), tensile stress (300–1000 MPa), and squareness ∼1.0, can result in unwanted perpendicular remanence. This can cause on-track erasure of the recorded data. One solution of this problem is to control the main pole remanence through the fabrication of a laminated (F/N) multilayer structure providing an antiferromagnetic coupling (AFC) between adjacent layers.

Since the thickness of a NiP nonmagnetic spacer layer should be very small, i.e. 2 to 5 nm, the most important requirement is to obtain the NiP spacer without a composition gradient at the CoFe/NiP interface. According to our data, if the P-content in the NiP film at the CoFe interface is smaller than 18 at. %, than NiP becomes magnetic. Therefore, through exchange coupling the whole multilayer becomes ferromagnetic, so that the advantage of AFC is lost. Importantly, it was observed that electrodeposited NiP, CoP, and NiCoP showed a gradient in composition with thickness, i.e. increase of P-content with increasing thickness of the deposit. Also, it was found that the composition gradient increases from 6.0 to 11 at. % P in NiP within a distance of 5.0 nm from the CoFe/NiP interface.

The present study describes the electrochemical synthesis of amorphous NiP alloys with 23–25 at. % P obtained from a designed plating solution in the presence of p-hydroxybenzhydrazide (p-HBHy) as an additive. The role of p-HBHy additive appeared to be essential in the electrodeposition of 2.0–5.0 nm amorphous NiP films without composition gradient. The electrochemical fabrication of a laminated CoFe/NiP nano structure for a perpendicular writer pole was carried out successfully in a dual-bath automated AMAT Raider electroplating tool.

The NiP single films were electrodeposited on 6 in round alumina coated ATIC wafers using 2000 Å sputtered copper seed layers (Cu-substrates) in a paddle cell. The NiP films were prepared from a plating solution containing: NiSO4 6H2O (65 g/l), NaCl (6 g/l), H3BO3 (25 g/l), H3PO4 (18 g/l), Na2-citrate (29.4 g/l), p-HBHy (0.6 g/l), and Na-lauryl sulfate (0.05 g/l). The solution pH was adjusted to 3.0 and galvanostatic electrodeposition was carried out at 1.5 mA/cm2 and solution temperature of 23 °C. The average thickness was obtained from nine point measurement distributed over the entire wafer surface. A DekTek profilometer was used to take the step height as thickness. The thickness uniformity of CoFe and NiP films defined as a σ/mean x 100 were optimized to <2% by optimizing the holder/wafer ratio currents density in the paddle cell. The films were deposited using the standard paddle configuration tool with a 1000 Oe external magnetic field. The agitation during electrodeposition was carried out by using a reciprocating paddle with motion rate of 150 mm/s. The agitation conditions resulted in a diffusion layer thickness of 50 μm for metallic ions, based on modeling calculation of Semitool Co. The volume of electrolyte in the paddle cell was 46 liters.

The electrodeposition of laminated (2.4T CoFe/NiP) multilayers was achieved using an automated tool (AMAT Raider, Semitool Co.-now Applied Materials) and dual-bath electrodeposition method. This system designed technique avoids a cross-contamination through effective rinsing after deposition of each 2.4 T CoFe magnetic and NiP nonmagnetic layer. It also enables to achieve very good thickness and...
composition uniformity. The plating solution at controlled pH 2.3 and conditions for electrodeposition of 2.4T CoFe layer were the same as described earlier.\textsuperscript{20}

Voltammetric experiments and electrodeposition at controlled potential using Pt-RDE were the same as described in Ref. 20.

The elemental composition and total weight of NiP films was determined by inductively coupled plasma optical emission spectroscopy (IC-OES) using a Teledyne Leeman Labs “prodigy” ISP spectrometer. NiP films were dissolved into approximately 5 ml solution of 50% (v/v) nitric acid and 1% (v/v) hydrochloric acid. The solutions were then diluted as necessary for analysis into volumetric flasks. The analysis of light elements in Ni films obtained from the plating solution in the presence of p-HBHy but without H$_3$PO$_3$, i.e. with 0.0 at. % P and NiP films were determined using dynamic secondary-ion mass spectrometry (SIMS) depth profile analysis. The SIMS analysis was obtained from Charles Evans & Associates through their in-house system.

The surface roughness of NiP films were measured using atomic force microscopy (AFM) operating ex-situ. The surface roughness, expressed as the root mean square (rms) was calculated for a scan area of $5 \times 5 \, \mu m^2$. The crystal structure was studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The magnetic properties were measured using a BH looper with low magnetic field of 100 Oe. The magnetic saturation flux density, $B_s$, was measured using BH looper with precision of $\pm 2\%$ due to the variability in the thickness/uniformity measurements. Stress was evaluated from measured changes in wafer curvature using the Stoney’s equation\textsuperscript{21} for the film on a stiff substrate.\textsuperscript{22}

**Results and Discussion**

*Influence of p-HBHy on voltammetric behavior.—* The cyclic voltammograms (Fig. 1) run in the solution with (red curve) and without (blue curve) presence of p-HBHy organic additive show three regions (a-c) corresponding to: (a) reduction of H$^+$ from the solution in the potential range from $-0.4$ to $-0.8 \, V/$SCE, (b) reduction of Ni$^{2+}$ and H$_3$PO$_3$ in the potential range from $-0.7$ to $-1.1 \, V/$SCE, and (c) oxidation of deposited NiP film in the potential range from $-0.4$ to $+0.2 \, V/$SCE, formed along the cathodic wave during the electrodeposition. The key difference between two voltammograms is the increase of a diffusion controlled peak (a) and the decrease of the anodic peaks (c) in the presence of p-HBHy in solution.

The plot of reversible peak potential-corresponding to the H$^+$ reduction (insert in Fig. 2-left) (i$_p$) vs. square root of the sweep rate ($\nu^{1/2}$) shown in Fig. 2-left was found to be linear, which means that the peak current of CV run in 0.1 M supporting electrolyte (SE) is diffusion controlled. By adding p-HBHy to the solution of SE the i$_p$ vs. $\nu^{1/2}$ slope increases. Figure 2-right shows the voltammograms obtained at the rotating disc electrode (RDE) at the Pt electrode obtained with (blue curve) and without (red curve) p-HBHy in deaerated SE solution. The limiting current of the RDE voltammogram-obtained in the presence of p-HBHy in SE solution-is larger than that one obtained without p-HBHy.

The higher concentration of H$^+$ observed in the presence of p-HBHy (Fig. 2) could be attributed to the higher supply of protons by p-HBHy additive to the electrode surface through the kinetic process described in Equations 1-3:

\begin{align*}
\text{p-HBHy}_{\text{sol}} + \text{H}^+ &\leftrightarrow \text{(p-HBHyH)$_{\text{sol}}$}^+ & \text{(1)} \\
\text{(p-HBHyH)$_{\text{sol}}$}^+ &\rightarrow \text{(p-HBHyH)$_{\text{ads}}$}^+ & \text{(2)} \\
\text{(p-HBHyH)$_{\text{ads}}$}^+ &\rightarrow \text{p-HBHy}^+_{\text{sol}} + \text{H}^+ & \text{(3)}
\end{align*}

The p-HBHy molecule is protonated in the acidic solution (Eq. 1) which diffuses to the electrode and gets adsorbed (Eq. 2). The protonated adsorbed (p-HBHyH)$_{\text{ads}}$ molecule dissociates at the electrode surface to the neutral molecule and proton (Eq. 3). The dissociation reaction is presumably shifted toward product formation due to the fast following reactions including an acid-base reaction and/or reduction of H$^+$ at the electrode surface.

Generally, high bulk concentration of protons is needed in the so called induced codoposition of NiP\textsuperscript{[23]} for the reduction of H$_3$PO$_3$ to phosphorus, regardless of the mechanism for incorporation of P into NiP film.\textsuperscript{24,25} i.e. direct reduction at the electrode (Eqs. 4, 5) or indirect reduction through formation of phosphine, PH$_3$, which reduces Ni$^{+2}$ ions (Eqs. 6, 7).

Direct mechanism.

\begin{align*}
\text{H}_3\text{PO}_3 + 2\text{e} + 2\text{H}^+ &\rightarrow \text{H}_2\text{PO}_2 + \text{H}_2\text{O} & \text{(4)} \\
\text{H}_2\text{PO}_2 + \text{e} + 2\text{H}^+ &\rightarrow \text{P (solid)} + \text{H}_2\text{O} & \text{(5)}
\end{align*}

Indirect mechanism

\begin{align*}
\text{H}_3\text{PO}_3 + 2\text{e} + 2\text{H}^+ &\rightarrow \text{H}_2\text{PO}_2 + \text{H}_2\text{O} & \text{(6)} \\
\text{H}_2\text{PO}_2 + 4\text{e} + 4\text{H}^+ &\rightarrow \text{PH}_3 (\text{gas}) + 2\text{H}_2\text{O} & \text{(7)}
\end{align*}

$2\text{PH}_3 (\text{gas}) + 3\text{Ni}^{+2} \rightarrow 2\text{P (solid)} + 3\text{Ni (solid)} + 6\text{H}^+$

[8]

The reactions-describing the mechanism-in Equations 4-8 are treated quantitatively. The detailed mechanism for the conversion of phosphorous acid to hypophosphorous acid occurring through 2e and 2H$^+$

![Figure 1. Cyclic voltammograms run in plating solution at pH 3.0 with (red curve) and without (blue curve) p-HBHy at Pt electrode (Area: 0.2 cm$^2$); Sweep rate: 20 mV/s.](image-url)
transfer-in terms of the sequence of these reactions (e, H+, e H+; e, e, H+,H+; H+, e, H+ etc.-) is not known. The ab initio MO study of reduction of phosphorous acid indicates that some of the protonation steps might be the rate limiting.26

Figure 3 shows results of the effect of the controlled electrode potential of Pt-RDE on the deposition of NiP films obtained from the plating solution containing p-HBHy organic additive. The current transients in Fig. 3-left show a decay with time, t, as $t^{-1/2}$ in the short period of time followed with the characteristic peak after which current falls to the steady state value. This peak is shifting to the longer time with less negative potential. The growth of NiP on an inert Pt substrate involves nucleation of centers (3D nucleation) at the initial time of deposition. The centers expand and coalesce to form monolayer deposit in two dimensional nucleation.27 Figure 3-right summarizes the results of P-content in NiP deposit and current efficiency as a function of electrode potential. The P-content in the NiP deposit stay at 23 at. % at the less negative potentials and decreases at the more negative potentials. The current efficiency has the opposite trend as a function of electrode potential.

Figure 4 exemplify E-t curves obtained at the constant current density (1.5 mA/cm²) obtained with and without p-HBHy present in the plating solution. The decay of potential from $-0.45$ V/SCE to about $-0.85$ V/SCE, reaching the characteristic peak potential after 500 seconds, obtained at Pt electrode in solution without p-HBHy, is shown as the 1st scan in Fig. 4-left. Since the current efficiency at Pt-RDE is very low the major discharging electroactive species is H+—which is reduced on Pt-RDE electrode at the half-wave potential, $E_{1/2} = 0.465$ V/SCE28—together with Ni$^{2+}$ species and H$_3$PO$_3$ which form 3D nucleation centers. The characteristic peak potential presumably corresponds to the 3D→2D nucleation transition reaching steady state potential when the platinum surface is fully covered with NiP layer, which is seen during 2nd scan at the formed NiP surface (Fig. 4-left).

The rate of decay is slower in solution without p-HBHy than with p-HBHy additive in solution (Fig. 4-right). That can indicate the faster coverage of NiP layer on Pt substrate with p-HBHy additive in solution.

Role of p-HBHy in electrodeposition of NiP films.—Figure 5-left shows the results of NiP film composition and plating rate, deposited on 200 nm Cu-seed layer on 6 in AlTiC wafers in solution containing p-HBHy, as a function of current density. The P-content in NiP
Figure 4. The potential-time (E-t) curves obtained from the plating solution with and without p-HBHy at the constant current density (i = 1.5 mA/cm²) at Pt-RDE (Area: 1 cm²); Rotation rate: 125 rpm. (Left) Plating solution without p-HBHy; The 1st scan was run on Pt-RDE and 2nd scan was run immediately after on deposited NiP layer during 1st scan. (Right) E-t curves run on Pt-RDE (Area: 1 cm²) with and without p-HBHy.

deposit increases in the range of current densities 0.3–1.5 mA/cm² and decreases at the current density > 1.5 mA/cm². It seems that both mechanisms are operating depending on applied current density, i.e. direct mechanism at CD > 1.5 mA/cm² and indirect mechanism at CD < 1.5 mA/cm². This conclusion is based on the results of a kinetic study of chemical reactions in NiP electrodeposition (see Fig. 1 in Ref. 25) which demonstrate that the indirect mechanism is favored at the low current density and direct mechanism at the higher current density. Figure 5-right shows the effect of thickness, from 2 to 200 nm, obtained at the current density of 1.5 mA/cm². The all compositions fell in the range of 23–25 at. %, which resulted with amorphous and nonmagnetic NiP films.

The obtained results demonstrate that amorphous and nonmagnetic NiP films with a very low thickness of 2–5 nm can be obtained by electrodeposition at low current density (1.5 mA/cm²), in acidic solution (pH 3.0) containing p-HBHy organic additive and with high concentration of H₃PO₃ (18 g/l) present in plating solution.

The high resolution TEM-EDS analysis of the elemental composition at the CoFe/NiP interface showed a sharp transition of elements at the interface (Fig. 6). The results of “zooming” sharp region at the interface (not shown here) demonstrated that inside of “sharp transition” from the bottom to the plateau of P-curve is less than 2 nm. That includes 3 measuring points since the spot size is 0.7 nm. Also, Auger in depth-profile of NiP at the NiP/Cu film interface (not shown here) demonstrated also a sharp transition at the Cu/ NiP interface.

Figure 7 shows the effect of H₃PO₃ concentration in the plating solution on the magnetic saturation, Bs, and composition of ~200 nm thick NiP films deposited on Cu-seed layer on 6 in AlTiC wafers, from the solution with (Fig. 7-right) and without (Fig. 7-left) p-HBHy organic additive. The galvanostatic deposition (i = 1.5 mA/cm²) from the solution without the presence of p-HDHy (Fig. 7-left) gives rise to a decrease of Bs-value from Bs = 0.59 T (Ni film with 0.0 at. % P) to Bs = 0.0 T (NiP film with 22 at. % P).

The addition of the p-HBHy additive into plating solution showed a dramatic effect on decrease of magnetic saturation and the change in composition as a function of H₃PO₃ concentration. The galvanostatic deposition (i = 1.5 mA/cm²) from the solution with p-HBHy (Fig. 7-right) gives rise to the decrease of Bs-value from Bs = 0.35 T (Ni film with 0.0 at. % P) to Bs = 0.0 T (NiP film with 22 at. % P). However, in order to obtain amorphous and nonmagnetic NiP film with 22 at. % P i.e. it was necessary to have only 5 g/l of H₃PO₃ in solution, compared to 20 g/l of H₃PO₃ as a source of phosphorus in
Figure 6. High resolution TEM-EDS analysis of CoFe/NiP interface. Scan conditions: Length: 80 nm; Time: 12 s; Spot size: 0.7 nm; Number of points: 160.

Figure 7. Effect of H$_3$PO$_3$ concentration in solution in the range of 0–20 g/l (Fig. 7-left) and in the range of 0–5 g/l on Bs value and composition of NiP deposit. Solution without p-HBHy additive. The comparison of results shown in Fig. 7-left and Fig. 7-right clearly demonstrate that under the same electrodeposition conditions using the lower H$_3$PO$_3$ concentration (5 g/l), the properties of NiP deposit—i.e. Bs = 0.0 T and P-content in deposit of 22 at%—are achieved in the presence of p-HBHy additive. This indicates that the reductive transformation H$_3$PO$_3$→ P at the electrode surface is more efficient due to the higher supply of protons by p-HBHy through the reactions in Equations 1–3.

It is important to note that the magnetic saturation for Ni film obtained in the presence of p-HBHy additive is not 0.59 T, but Bs = 0.35 T. Such a decrease of the magnetic saturation of Ni film is due to the incorporation of nonmagnetic light elements or “impurities” such as O, C, N, P, etc. in Ni ferromagnetic film.

SIMS analysis of included light elements in Ni and Ni$_{78}$P$_{22}$ deposited films obtained from the solution containing p-HBHy organic additive is presented in Table I. The origin of carbon, nitrogen and hydrogen is certainly from the inclusion of organic compounds present in electrolyte or their reduction by-products. Notably, we have found that the molecules of organic additives and their reduction products were incorporated into the deposit by dissolution of deposit and HPLC analysis of the obtained solution. 30,31 The origin of S, Cl, and B comes from anions present in electrolytes which are presumably complexed with Ni$^{2+}$ ions forming neutral salts. The origin of oxygen is from organic compounds present in plating solution and from NiOH, Ni(OH)$_2$ and NiO, which are formed possibly through mechanism discussed in our recent paper. 29 The total amount of light elements present as “impurities” is much higher in Ni (4.23 at. %) than in Ni$_{78}$P$_{22}$ film (0.276 at. %), which means that NiP film is very pure.

| Film      | O    | H    | C    | N    | S     | Cl     | B   |
|-----------|------|------|------|------|-------|--------|-----|
| Ni        | 1.76 | 1.65 | 0.79 | 0.0057 | 0.0132 | 0.016 | Traces |
| Ni$_{78}$P$_{22}$ | 0.078 | 0.14 | 0.055 | 0.0002 | 0.0012 | 0.002 | Traces |

Table I. SIMS analysis of light elements in atomic % of Ni and NiP films obtained in the presence of p-HBHy additive.

Dual-bath electrodeposition technique of (CoFe/NiP)$_n$ multilayer.—Electrodeposition of F/N multilayer from the single electrolyte solution, i.e. single-bath techniques, containing noble metal ions (Cu$^{2+}$, Au$^+$, Pt$^{+2}$ etc.) used for N-layer and ferromagnetic metal ions (Ni$^{2+}$, Co$^{2+}$, Fe$^{2+}$) as F-layer have been reviewed. 32 The electrode potentials are well separated and N-layer can be obtained as a pure noble metal. However, it is not possible to produce a layer of pure ferromagnetic metal or alloy without inclusion of noble metal. Notably, electrodeposition of (CoFe/NiP) multilayer cannot be done from the single electrolyte solution, indicated by results shown in Fig. 3-left.
The dual-bath technique for electrodeposition of Ni/NiP multilayer from two separated plating solutions, by moving the substrate from one to another solution, was demonstrated earlier, although some problems were encountered relating to the cleaning the substrate and contaminating Ni plating solution. In this work, electrodeposition of CoFe/NiP multilayer nano structure was achieved using an automated plating tool in which the wafer substrate was transferred from the CoFe solution to H2O rinsing, then to NiP solution and then H2O rinsing again. The electrodeposition of each layer was carried out using the constant current density under optimized conditions, including their current density, plating rate, composition and thickness uniformity.

Figure 8-left illustrates electrodeposition of (CoFe/NiP)n multilayer with n = 19 periods, using dual-bath techniques. The ferromagnetic layer is ∼40 nm thick 2.4T CoFe film which is crystalline with bcc crystal structure. The 2.4T CoFe deposited in F/N multilayer showed much smaller grain size (TEM in Fig. 1-left) compared to the thick 2.4T film (not shown here). The amorphous and nonmagnetic NiP layers are ∼3.0 nm thick. Both deposited layers grew parallel to the Cu-substrate with good uniformity and without curvatures.

The electrodeposited multilayer film (Fig. 8-right) showed excellent anisotropic (Mh/Me ∼0.0) and soft magnetic properties with easy axis coercivity (Hex,E = 1.6 Oe) and hard axis coercivity (Hex,H = 0.3 Oe). The squareness (Mh/Mh) is defined as a ratio of remanence magnetization (Mr) of the hard axis coercivity and saturation magnetization (Ms) of the easy axis coercivity at the magnetic field equal zero. These soft magnetic properties are very desirable for writer pole application. In addition, the F/N multilayer nano structure can control writer remanence and prevent the occurring of erasure after write (EAW). Generally, the coercivity is a material and thickness dependent magnetic property. In Table II are listed the properties of related ferromagnetic materials for the purpose of comparison. The coercivity and squareness are reduced in 2.4T CoFe layer laminated with NiP.

| Material | No. periods | Thickness (nm) | Hex,E (Oe) | Hex,H (Oe) | Hk, (Oe) | Mr/Ms  |
|----------|-------------|----------------|-------------|-------------|---------|--------|
| CoFe*    | -           | ~500           | 25          | 12          | 20      | 0.9    |
| (CoFe* /NiP)n | 8         | ~500           | 12          | 2.0         | 20      | 0.1    |
| (CoFe* /NiP)n | 19     | ~800           | 1.6         | 0.3         | 25      | ~0.0   |

*CoFe with Bs = 2.4 T
nonmagnetic spacer. The number of periods, n, further improves magnetic properties.

**Morphology, structure, stress, and roughness of NiP films.**—Figure 9-left shows a TEM cross-section of an electrodeposited Ni$_{78}$P$_{22}$ film, with a compact amorphous structure on Cu-seed layer used as a substrate. It is important to note that electrodeposited amorphous NiP films were found to form a composition-modulated layered structures, striations, or lamellar contrasts running parallel to the substrate. Figure 9-right exhibits the conformal electrodeposition of ~200 nm Ni$_{78}$P$_{22}$ film deposited through a lithographic mask over CoFe write pole.

Figure 10 shows typical XRD diffraction patterns of Ni and Ni$_{78}$P$_{22}$ films obtained in plating solution with p-HBHy additive. As deposited Ni films (Fig. 10a) showed the crystalline structure with fcc (111) and (200) peaks. As deposited Ni$_{78}$P$_{22}$ film (Fig. 10c) showed the typical shape of XRD amorphous structure without peaks. Annealing temperature of 280°C through 2 hours did not induce the crystallization of the amorphous Ni$_{78}$P$_{22}$ layer (Fig. 10c). TEM cross-section of Ni$_{78}$P$_{22}$ film after annealing (not shown here) confirmed our conclusion.

Figure 11 illustrates the effect of P-content in the deposit from P = 0.0 at% (Ni film) to P = 22 at% (Ni$_{78}$P$_{22}$ film) on stress (Fig. 11-left) and roughness (Fig. 11-right). The Ni films, obtained without H$_3$PO$_3$, in the plating solution, showed the high tensile stress of 610 MPa. The addition of p-HBHy into plating solution resulted with Ni film with a lower tensile stress of 450 MPa. The decrease of tensile stress in Ni film can be attributed to the codeposition of light elements from p-HBHy molecule; presumably at the grain boundaries (see SIMS results in Table I). The increase of P-content, by adding H$_3$PO$_3$ into the plating solution, gave rise to a decrease of tensile stress of the films changing from crystalline (Ni, Ni$_{89}$P$_{11}$) to amorphous NiP films with P > 18 at%. The similar stress behavior of NiP deposits were reported as plotted stress against the phosphorus content.

One of the most common origin of the residual stress in electrodeposited films is the incorporation of hydrogen at the grain boundaries in the form of metal hydrides (adsorption) and subsequent diffusion out as a hydrogen molecule (desorption) leaving vacancies at the grain boundaries in the deposit. The decrease of tensile stress in NiP films with increase of P-content was explained through several theories including: adsorption/desorption of hydrogen, crystallite joining, and combined effects of texture and hydrogen adsorption/desorption.

The p-HBHy additive acts as a stress reliever and smoothening agent decreasing of roughness of Ni film (P = 0.0 at%) (Fig. 11-right). The increase of P-content in the NiP deposit brings about further decrease of rms roughness. The amorphous ~200 nm thick NiP films with P > 18 at% are very smooth with \( \text{rms} = 1.3–1.4 \) nm measured by atomic force microscopy (see Insert in Fig. 11-right).

**Conclusions**

1. The obtained results demonstrate that amorphous and nonmagnetic NiP films with very low thickness from 2 to 5 nm, used as nonmagnetic spacer, in a laminated CoFe/NiP nano structure, can be obtained by electrodeposition at low current density in acidic plating solution containing p-HBHy organic additive and H$_3$PO$_3$.
2. The role of p-HBHy additive is essential in electrodeposition of 2–5 nm amorphous NiP films without composition gradient. The higher concentration of H$^+$ observed in the presence of p-HBHy, which is necessary for the reductive transformation of H$_3$PO$_3$ to the elemental phosphorus, could be attributed to the higher supply of protons by p-HBHy additive to the electrode surface through the kinetic process.
3. The presence of p-HBHy in plating solution brings about faster surface coverage of NiP layer on CoFe substrate, as well as the...
improvement of morphology, stress and roughness of amorphous NiP films.

4. The electrodeposition of a (2.4T CoFe/NiP) multilayer nanostructure was achieved, using dual-bath technique and automated plating tool, showing the excellent anisotropic and magnetic properties, which were desirable for application in the recording heads as a laminated write pole.

References

1. Y. Okinaka and T. Osaka, “Electroless Deposition Process: Fundamentals and Applications”, Eds. H. Gerischer and C. W. Tobias in Advances in Electrochemical Science and Engineering, VCH, New York (1990) p. 55.
2. E. Bredael, B. Blanpain, J.-P. Celis, and J.-R. Ross, J. Electrochem. Soc., 141, 294 (1994) and references therein.
3. E. Toth-Kadar, I. Bakonyi, A. Solyom, J. Hering, and G. Konczos, Surf. Coat. Technol., 31, 311987 and references therein.
4. A. Revesz, L. Lenvai, J. Loranth, and I. Bakony, J. Electrochem. Soc., 148, C715 (2001).
5. M. Saavudi, E. Chassing, M. Cherkami, and M. Ebutonhami, J. Appl. Electrochem., 32, 1331 (2002).
6. M. Sun, S. Riemer, M. Kief, and I. Tabakovic, ECS Trans., 16, 177 (2009).
7. J. P. Carini, S. R. Nagel, L. K. Varga, and T. Schmidt, Phys. Rev., B27, 7589 (1983).
8. I. Paseka, Electrochim. Acta, 47, 921 (2001).
9. J. Y. Song and J. Yu, Thin Solid Films, 415, 167 (2002).
10. M. H. Seo, J. S. Kim, W. S. Hwang, D. J. Kim, S. S. Hwang, and B. S. Chun, Surf. Coat. Technol., 176, 135 (2004).
11. C. S. Lin, C. Y. Lee, F. J. Chen, and W. C. Li, J. Electrochem. Soc., 152, C370 (2005).
12. L. Wang, Y. Gao, Q. Xue, H. Liu, and T. Xu, Surf. Coat. Technol., 200, 3719 (2006).
13. M. Ratzker, D. S. Lashmore, and K. W. Pratt, Plating Surf. Finish, 74 (1996).
14. L. Wang, Y. Gao, T. Xu, and Q. Xue, Appl. Surf. Sci., 252, 7361 (2006).
15. I. Bakonyi, A. Burgstaller, W. Socher, J. Voitlander, E. Toth-Kadar, A. Loves, H. Ebert, E. Wachtel, N. Willman, and N. H. Liebermann, Phys. Rev., B 47, 14961 (1993).
16. T. Osaka and I. Kowata, J. Metal Finish Soc. Jpn., 34, 330 (1983).
17. M. Kief, V. Inturi, M. Benkali, I. Tabakovic, M. Sun, O. Heinonen, S. Riemer, and V. Vas’ko, IEEE Trans. Mag., 44, 113 (2008).
18. S. S. Djokic, J. Electrochem. Soc., 146, 1824 (1999).
19. Y. Kanada and H. Yazawa, US Pat. No. US 6,600,629 B2 (2003).
20. S. Riemer, J. Gong, M. Sun, and I. Tabakovic, J. Electrochem. Soc., 156, D439 (2009).
21. G. C. Stoney, Proc. R. Soc. Lond. Ser., A, 82, 172 (1909).
22. I. Tabakovic, J. Gong, S. Riemer, V. Venkatasamy, and M. Kief, Electrochim. Acta, 55, 9035 (2010).
23. A. Bremner, “Electrodeposition of Alloys” Vol. 2, p. 347, Acad. Press, New York (1963).
24. T. Harris and Q. D. Dang, J. Electrochem. Soc., 140, 81 (1993).
25. M. Saitou, Y. Okudaira, and W. Oshikawa, J. Electrochem. Soc., 150, C140 (2003).
26. G. Cui, N. Li, J. Zhao, and M. Zhang, J. Electrochem. Soc., 152, C861 (2005).
27. D. Fletcher, R. Geef, R. Pest, L. M. Peter, and J. Robinson, “Instrumental Methods in Electrochemistry”, Horwood Publishing Ltd, England, 1985, p. 298.
28. I. Tabakovic, S. Riemer, N. Jayaraju, V. Venkatasamy, and J. Gong, Electrochim. Acta, 58, 25 (2011).
29. R. C. O’Handley, “Modern Magnetic Materials” John Welley & Sons, New York, p. 391.
30. I. Tabakovic, S. Riemer, K. Tabakovic, M. Sun, and M. Kief, J. Electrochem. Soc., 153, C586 (2006).
31. I. Tabakovic, S. Riemer, J. Gong, V. Venkatasamy, S. Axdal, and M. Kautzky, Electrochim. Acta, 119, 49 (2014).
32. I. Bakony and L. Peter, Progress in Material Science, 55, 107 (2010).
33. C. A. Ross, L. M. Goldmann, and F. Speapen, J. Electrochem. Soc., 140, 91 (1993).
34. K. Nakamoto, T. Okada, H. Hoshiya, N. Yoshida, Y. Kawat, M. Hatatani, Y. Okada, H. Kimura, M. Mochizuki, K. Kusukawa, C. Ishikawa, and M. Fuyama, J. Electrochem. Soc., 146, 1824 (1999).
35. R. L. Zeller and U. Landau, J. Electrochem. Soc., 138, 1010 (1991).
36. R. Weil, Plating, 58, 137 (1971).
37. L. Chang, C.-H. Chen, and H. Fang, J. Electrochem. Soc., 155, D57 (2008).