Effects of cathode rotation and substrate materials on electrodeposited CoMnP thick films

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Abstract
In this study, rotating-cathode electrodeposition was performed to deposit 30 μm thick CoMnP films on various substrate materials at room temperature. The electrodeposition configuration and parameters realized a constant current efficiency of about 95%, which was under activation control rather than mass-transport control. Compositional analysis indicated that the deposited thick films were Co-rich with a Co content 92–95 wt.%, regardless of deposition parameters. X-ray diffraction revealed that cathode rotation physically altered the preferred orientation of Co crystallites. The texture of Co crystallites changed with the cathode rotational speed from distinct hexagonal close-packed (HCP) (002) to a heterogeneous phase mixture of HCP (110) and face-centered cubic (FCC) (220). The substrate materials physicochemically affected the relationship between rotational speed and microstructural evolution. The microstructural texture changed nonlinearly with the cathode rotational speed when the films were deposited on catalytic substrate materials, suggesting a substantial influence of the substrate activation nature. Due to magnetocrystalline anisotropy, the resultant films exhibited hard magnetic properties while depositing at the optimal cathode rotational speed. Stationary-cathode electrodeposition resulted in rough CoMnP films with Co grains of 8–18 nm and high Mn content. These films exhibited unique in-plane magnetic properties compared with the films deposited with electrolyte agitation. This study is the first to investigate the combined effects of cathode rotational speed and the activation nature of substrates on the growth behavior of electrodeposited Co-rich CoMnP thick films. The results can be extended to electrodeposition of other Co-based alloys, such as CoP, CoNiP, CoWP, CoPtP, and CoNiMnP.

1. Introduction

Electrodeposited films made of Co-based alloys (e.g., CoP, CoNiP, CoMnP, CoWP, CoPtP and CoNiMnP) are promising for use in microelectromechanical systems (MEMS) [1–7]. The magnetic properties of such alloys depend strongly on the Co content, grain size, and crystalline texture and therefore magnetocrystalline anisotropy (MA) of the Co crystallites [8]. Furthermore, electrodeposited Co-rich alloys have hard magnetic properties that originate from the fine Co grains isolated by the nonmagnetic elements segregated along grain boundaries [6, 7, 9–11]. Therefore, the electrodeposition parameters are crucial to achieving the hard magnetic properties of Co-rich alloy films [12].

Electrodeposition deposition possesses the following advantages: low processing temperatures, low process cost, high scalability, and compatibility with microfabrication. The chemical bath formula and physical setup are critical electrodeposition parameters. Furthermore, electrolyte agitation and the substrate materials considerably affect the nucleation and growth kinetics of Co crystallites, thereby influencing the composition and microstructure of electrodeposited films [9, 12]. Agitation methods such as air bubbling and cathode rotation can remove the gaseous hydrogen produced by reduction reactions on cathode surfaces [13, 14].
substrates were polished to a same status prior to powder, degreasing, rinsing, and pickling prior to electrodeposition and electroless deposition. All of the we followed the typical substrate pretreatment steps, which include grinding to 4000 grit, polishing with Al₂O₃

2.1. Rotating-cathode electrodeposition

Agitation also prevents anomalous codeposition by reducing the polarization and barrier layer of hydrogen adatoms on cathode surfaces [13, 14].

Cathode rotation can couple with other electrodeposition parameters to obtain various film compositions and microstructures [15–17]. Walsh et al demonstrated that with minimal nucleation effect, crystal growth behavior can be electrochemically controlled through rotating cylindrical electrode (RCE) electrodeposition [18]. Under complete mass-transport control, cathode rotational speed and growth behavior are related. However, few studies have investigated the combined effects of active surfaces of substrate material and cathode rotation on the growth behavior of deposited films. In a cobaltic electrolyte, the activation nature of a substrate originates from the extent of inducing electro-oxidation reactions, replacement reactions and surface oxidation/passivation [19, 20]. Moreover, according to Walsh et al [18], thick films, which are typically required in end applications for hard magnetic films [21, 22], are ideal for electrodeposition studies because of their steady-state growth. Composition can probably be independent of the film thickness for thick films [23]. Therefore, we studied the compositions, crystallographic structures and magnetic properties of Co-based thick films electrodeposited on substrate materials with various activation natures through rotating-cathode electrodeposition.

We conducted rotating-cathode electrodeposition (without additional air bubbling) in an acidic electrolyte bath and deposited 30 μm thick CoMnP films on various substrates at room temperature. CoMnP was selected as model sample out of Co-based alloys. The cobaltic ion concentration was stabilized in the bulk electrolyte solution using a soluble anode of electrolytic Co pieces. To realize a well-controlled mass-transport limitation, high concentrations of cobaltic ions and the reduction agent along with low applied current density (CD, fixed at 5 mA cm⁻²) were adopted. Systematic and comparative investigations were conducted in terms of rotational speed of the cathode, substrate (i.e., cathode) material effects and agitation methods. Substrate materials including Cu, electroless-deposited CoP thin films on Cu (referred to as CoP/Cu), and low carbon steel (S20C, according to Japanese Industrial Standards) were used to study the effects of different active surfaces. For comparison, we performed stationary-cathode electrodeposition with electrolyte agitation through air bubbling. We paid special attention to the rotation-speed dependent evolution of microstructural textures and the resulting hard magnetic properties for the resultant films.

2. Experimental details

2.1. Rotating-cathode electrodeposition

We followed the typical substrate pretreatment steps, which include grinding to 4000 grit, polishing with Al₂O₃ powder, degreasing, rinsing, and pickling prior to electrodeposition and electroless deposition. All of the substrates were polished to a same status prior to film deposition. The area (A) and thickness of the substrates were 1.5 cm × 2.5 cm and 2 mm, respectively. The Cu substrate served as a simple conductive cathode, whereas the CoP/Cu played a texture-inducing role for subsequent electrodeposition [12]. Because Co (−0.277 V relative to the standard hydrogen electrode [SHE] potential) is more electropositive than Fe (−0.44 V relative to the SHE potential) [19], the S20C substrate was considered the catalytic surface in this study. The S20C substrate was used after the typical annealing and decarburization processes, and comprised abundant α-ferrite grains. Annealing can diminish the effect of substrate strain on electrodeposited films [24]. Note that nonmagnetic Fe-

### Table 1. Bath composition and depositing parameters for rotating-cathode electrodeposition of CoMnP thick films [6, 7].

| Component                  | Concentration (molar) |
|----------------------------|-----------------------|
| CoCl₂ · 6H₂O               | 0.42                  |
| CoSO₄ · 7H₂O               | 0.053                 |
| MnCl₂ · 4H₂O               | 0.4                   |
| NaH₂PO₂ · H₂O             | 0.2                   |
| NH₄Cl                      | 1.8                   |

| Deposition parameters      |
|----------------------------|
| Bath volume                | 2000 ml               |
| pH value                   | 3.7                   |
| Current density (CD)       | 5 mA cm⁻²             |
| Temperature (°C)           | 25                    |
| Depositing time (min)      | 300                   |
based substrate such as austenitic steel is non-catalytic to cobaltic electrolyte. Austenitic steel comprises of high contents of Ni, N and Cr, and forms passivated CrO film on the substrate surface.

Tables 1 and 2 respectively present the bath compositions and depositing parameters for electrodeposition of CoMnP thick films and electroless deposition of CoP thin films. Details of the procedure used for the electroless deposition of the CoP films on the Cu substrate can be found in [9]. The thickness of the CoP in this study was 0.5 μm. The deposition time (t) for all film samples was 300 min. For each electrodeposition configuration, we deposited two or more replicate samples. For comparison, we performed additional electrodeposition without cathode rotation but with air bubbling agitation at a gas flow rate of approximately 2 L min⁻¹ on each substrate material.

We used a servomotor mounted atop an electrodeposition cell to control cathode rotation (figure 1(a)). A rotation cycle comprised one 360° clockwise rotation and one 360° counterclockwise rotation. The maximum rotational speed was 180 rpm. Electrolytic Co pieces wrapped in insoluble Ti meshes were used as anodes. A custom annular holder composed of polymers was used for fastening and accessing the substrate, as shown in figure 1(b). The distance between the anode and cathode was 4.0 cm for all electrodeposition procedures.

2.2. Materials characterization
The compositions of the deposited films were characterized using a Hitachi S3400N scanning electron microscope (SEM) equipped with a calibrated energy-dispersive x-ray spectrometer (EDS). A profilometer (Mitutoyo SJ-310, Japan) was used to measure film thicknesses from the areas of boundary steps between the CoMnP film and the substrate. Current efficiency (CE) was estimated using the measured film thickness as
The theoretical deposit thickness from all of the electrodeposition parameters are the same. The median thickness of the approximately 5 wt.%, regardless of the electrodeposition parameters. In addition, the Co content of 92 wt.%. Furthermore, the Mn content in the film was 0.5–2.3 wt.%, and the P content was approximately 5 wt.%, regardless of the electrodeposition parameters. In addition, the film thickness resulted from all of the electrodeposition parameters are the same. The median thickness of the films was 29.5 μm based on measured results. The theoretical deposit thickness (θtheo) was calculated using Faraday’s Law by using the following expression [26]:

\[
\text{CE} = \frac{W_{\text{Co}}}{W_{\text{theo}}}
\]

where \( W_{\text{Co}} \) is the weight of Co actually deposited, and \( W_{\text{theo}} \) is the theoretical weight when all the applied current are for complete reduction of Co. Because the electrodeposited films in this study were uniform and Co rich (tables 3–5), we used film thickness as a proxy for weight to estimate CE. The surface morphological characteristics and arithmetical average roughness (Ra) of the films deposited on the Cu substrates were analyzed through atomic force microscopy (AFM) with an NS4/D3100CL/MultiMode microscope (Digital Instruments) in tapping mode. A Bruker Dimension FastScan was operated in tapping mode to analyze the films deposited on the Cu substrates. The AFM images were 20 μm × 20 μm and had a resolution of 512 × 512 pixels. A Bruker D8 x-ray diffractometer (XRD) with \( \theta - 2\theta \) configuration and Cu Kα radiation (wavelength \( \lambda = 1.5406 \) Å) was used to identify crystallographic microstructures and textures. Magnetic properties were measured at room temperature with a Lake Shore 7407 vibrating sample magnetometer (VSM) and a maximum applied field of 12 kOe. The VSM was used to characterize only the films on the nonmagnetic copper and CoP/Cu substrates and not those on the ferromagnetic S20C substrates. The magnetic properties of CoMnP films on S20C substrates can be reflected by MA of microstructures according to XRD results, which are discussed later in this article.

### 3. Results and discussion

#### 3.1. Compositional and morphological analysis

The compositions of the deposited films are presented in tables 3–5. All of the CoMnP films were Co rich, with a Co content of 92–95 wt.%. Furthermore, the Mn content in the films was 0.5–2.3 wt.%, and the P content was approximately 5 wt.%, regardless of the electrodeposition parameters. In addition, the film thickness resulted from all of the electrodeposition parameters are the same. The median thickness of the films was 29.5 μm based on measured results. The theoretical deposit thickness (\( \theta_{\text{theo}} \)) was calculated using Faraday’s Law by using the following expression [26]:

### Table 3. EDS results of deposited films on copper substrates at different rotational speeds. Comparative results are from stationary cathode with air bubbling agitation. Data reported with one standard deviation.

| Element | 0 rpm | 15 rpm | 45 rpm | 60 rpm | 120 rpm | Air bubbling |
|---------|-------|--------|--------|--------|---------|-------------|
| Co      | 92.3 ± 2.6 | 94.7 ± 2.8 | 94.4 ± 2.8 | 94.3 ± 2.7 | 94.4 ± 2.7 | 94.1 ± 2.7 |
| Mn      | 2.3 ± 0.1  | 0.5 ± 0.1  | 0.5 ± 0.1  | 0.5 ± 0.1  | 0.6 ± 0.1  | 0.8 ± 0.1   |
| P       | 5.4 ± 0.2  | 4.8 ± 0.2  | 5.1 ± 0.2  | 5.2 ± 0.2  | 5.0 ± 0.2  | 5.1 ± 0.2   |

Unit: weight percentage.

### Table 4. EDS results of deposited films on CoP/Cu substrates at different rotational speeds. Comparative results are from stationary cathode with air bubbling agitation. Data reported with one standard deviation.

| Element | 0 rpm | 15 rpm | 45 rpm | 60 rpm | 120 rpm | Air bubbling |
|---------|-------|--------|--------|--------|---------|-------------|
| Co      | 93.4 ± 2.9 | 94.6 ± 3.0 | 94.8 ± 2.8 | 94.5 ± 3.3 | 94.8 ± 2.7 | 94.4 ± 3.0 |
| Mn      | 1.9 ± 0.1  | 0.7 ± 0.1  | 0.5 ± 0.1  | 0.5 ± 0.1  | 0.5 ± 0.1  | 1.0 ± 0.1   |
| P       | 4.7 ± 0.2  | 4.7 ± 0.2  | 4.7 ± 0.3  | 5.0 ± 0.3  | 4.7 ± 0.2  | 4.6 ± 0.2   |

Unit: weight percentage.

### Table 5. EDS results of deposited films on S20C substrates at different rotational speeds. Comparative results are from stationary cathode with air bubbling agitation. Data reported with one standard deviation.

| Element | 0 rpm | 30 rpm | 60 rpm | 120 rpm | Air bubbling |
|---------|-------|--------|--------|---------|-------------|
| Co      | 93.6 ± 2.7 | 94.5 ± 2.8 | 94.3 ± 2.7 | 94.2 ± 2.7 | 94.3 ± 2.7 |
| Mn      | 1.4 ± 0.1  | 0.5 ± 0.1  | 0.6 ± 0.1  | 0.6 ± 0.1  | 0.5 ± 0.1   |
| P       | 5.0 ± 0.3  | 5.0 ± 0.2  | 5.1 ± 0.2  | 5.2 ± 0.2  | 5.2 ± 0.2   |

Unit: weight percentage.
where $\rho$ is the density of Co, $A$ is the depositon area, $m$ is the valence number of the cobaltic ion, $F$ is the Faraday constant, $A_{\text{wt}}$ represents the atomic weight of Co, and $I$ denotes the total applied current in the process. In the electrodeposition process, the product of applied current and deposition time ($t = 1800$ s) equals the total cathodic charge, which was 337.5 C in this study. The estimated $\delta_{\text{theo}}$ was 30.9 $\mu$m, and the CE was calculated using the measured film thickness (29.5 $\mu$m) and $\delta_{\text{theo}}$. The CE was approximately 95% for all electrodeposition in this study.

However, for the stationary-cathode electrodeposition without air bubbling (referred to as 0 rpm), two features of the compositions of the films on all substrate materials were distinct from those deposited with the rotating cathode (tables 3–5). First, the Co content of the 0 rpm films was 1–2 wt.% lower than that of the films deposited with the cathode rotating at any speeds. Second, the Mn content was 1–2 wt.% higher than that of the
films deposited with the rotating cathode. These two distinct features are consistent with the low Mn content (0.5–1.0 wt.%) of the stationary-cathode deposited films using air bubbling agitation. These results indicated a deposition process similar to the anomalous codeposition of the Co\(^{2+}\) and Mn\(^{2+}\) species due to polarization during poor agitation \[16\]. The rate-determining step resulted in the same CE, regardless of the substrate material, rotational speed and agitation method. Thus, the diffusion control due to the concentration difference in the bulk solution was negligible during rotating-cathode electrodeposition. Configurations such as the rotating cathode and RCE that generate effective agitation, uniform current distribution, and high throwing power assist to relieve the mass transport limitation at the deposition interface \[27–29\].

Figure 3. AFM images of the CoMnP films deposited on CoP/Cu substrates with different rotational speeds without additional bath agitation: (a) 0 rpm, (b) 15 rpm, (c) 45 rpm, (d) 60 rpm, (e) 120 rpm, and (f) stationary cathode with air bubbling. The roughness values (Ra) are shown accordingly. All images are based on a scan area of 20 \(\mu\text{m} \times 20 \mu\text{m}$. 
The AFM images in figure 2 illustrate the morphological features of the CoMnP films deposited on the Cu substrate. The roughness of the polished Cu substrate was $Ra = 5.1 \pm 0.9 \text{ nm}$ prior to electrodeposition. Numerous nodules and bulges formed after stationary-cathode electrodeposition (figure 2(a)). Electrolyte agitation using cathode rotation and air bubbling reduced the roughness of the resultant films ($Ra = 13.5–18.2 \text{ nm}$). Similar behaviors were observed for the films deposited on the CoP/Cu substrates (figure 3). The surface bulges were considerably larger than those of the films deposited on the Cu substrates. The $Ra$ of CoP films on Cu substrates was in the tens of nanometers [9]. Cathode rotation accelerated the lateral growth of clusters and bumps on the surface during electrodeposition. Therefore, the surface roughness decreased as demonstrated in [30]. However, in the case of electrodeposition without electrolyte agitation, anomalous codeposition was responsible for the large surface bulges of the resultant films. The reduction potentials of $Co^{2+}$ and $Mn^{2+}$ species are $-0.277 \text{ V}$ and $-1.185 \text{ V}$, respectively, with respect to the SHE potential in aqueous electrolyte. Polarization caused by the lack of electrolyte agitation resulted in a favorable interface for $Mn^{2+}$ reduction [16]. In addition, comparing to samples deposited with electrolyte agitation, the 0 rpm samples exhibited unique magnetic properties (discussed later in this article). The CoMnP films on the CoP/Cu substrates and the 0 rpm samples were in a different level of surface roughness. The morphological features of the CoMnP films on the S20C substrates were similar to those on the Cu substrates (results not shown).

3.2. Analysis of microstructure

XRD results in figure 4 illustrate the evolution of the crystallographic microstructures of the films with the rotational speed and agitation method on different substrate materials. For the films deposited at 15 rpm on the Cu substrates, a distinct HCP (002) texture was observed after rotating-cathode electrodeposition (figure 4(a)). A higher rotational speed resulted in a more heterogeneous mixture of hexagonal close-packed (HCP) (110) and face-centered cubic (FCC) (220). Distinct texture of HCP (110) and FCC (220) were obtained when the cathode rotational speed was $\geq 45 \text{ rpm}$. Deconvolution of the XRD patterns for the HCP (110) and FCC (220) signals revealed that the partially overlapping peaks at high diffraction angles did not result from the $K\alpha_2$ irradiation of the Cu target.
For the films deposited on the CoP/Cu substrates (Figure 4(b)), the microstructure changed more drastically with the rotational speed than it did for those on the Cu substrates. Pre-electroless deposited CoP thin films comprised Co-rich nanocrystallites and exhibited distinct HCP (100), HCP (101) and HCP (110) microstructures and a minor HCP (002) microstructure because of faulty stacking along the c-axis [9, 31]. The electroless-deposited CoP thin films functioned as a texture-inducing underlayer [12]. Therefore, substantial HCP (110) and FCC (220) microstructures were expected because the deposition conditions favored the coexistence of the two textures. The CoMnP alloy electrodeposited on the S20C substrates exhibited a gradual evolution from the HCP (002) texture to the heterogeneous HCP (110) and FCC (220) mixture when increasing the cathode rotational speed of (Figure 4(c)). With the assistance of air bubbling agitation, more heterogeneous HCP (110) and FCC (220) texture appeared in films deposited with and without cathode rotation. Such different texture evolutions resulted from the intrinsically stronger activation nature of the Fe substrate than that of the Cu and Co substrates for the reduction of cobaltic ions [21]. We confirmed that deposition time (i.e., film thickness) did not affect the composition or crystallographic microstructure in a studied range of 200–600 min (data not shown). Figure 4 indicates that the activation nature of the substrate materials crucially affects the nucleation and growth behavior of Co crystallites and thus their textures.

We used the following equation for the texture coefficient (TC) to study the effect of cathode rotation on the preferred orientation of the deposited CoMnP films [32]:

$$TC(hkl) = \frac{I(hkl)}{\sum_{i=1}^{n} I_i(hkl)} I_0(hkl)$$

where $I_0(hkl)$ represents the diffraction intensity of crystal plane (hkl) from the Joint Committee on Powder Diffraction Standards (JCPDS) card, $I(hkl)$ is the diffraction intensity of crystal plane (hkl) on the XRD pattern of the deposits, and $n$ is the number of diffraction peaks. Here, $TC(hkl)$ represents the extent of the preferred orientation for microstructure with crystal plane (hkl) parallel to the surface of the CoMnP film. Note that the peak intensities between HCP and FCC microstructures are relative in the present study.

Figure 5 illustrates the evolution of the TC with the rotational speed of the cathode. At low rotational speeds, the nucleation and growth of crystallites are mostly undisturbed. Therefore, the films on all three substrate materials exhibited strong preference for the HCP (002) orientation, which was the most densely packed lattice
plane being parallel to the surface of deposited film [15]. At a high rotational speed (120 rpm here), both the surface diffusion and adsorption behavior of the adatoms were physically disturbed [14–16], yet the deposition rate was unaltered chemically. Therefore, an identical heterogeneous phase composed of highly textured HCP (110) and FCC (220) Co crystallites was obtained regardless of the substrate material. The transition region of TC from HCP (002) to the mixture of HCP (110) and FCC (220) was wider for the CoMnP films on the Cu substrates and narrower for the films on the CoP/Cu substrates (figures 5(a) and (b)). The rough surface of CoP/Cu substrates inhibited the disturbance of fluid shear at the metal-solution interface caused by cathode rotation when a moderate speed of cathode rotation was used [18]. For the films on the Cu and CoP/Cu substrates, the transition behavior changed linearly with increasing the rotational speed because of the boundary layer thickness linearly decreased. By contrast, the Fe of the S20C substrate was catalytic for the reduction of cobaltic ions. The high surface concentration of Co adatoms predominated over the boundary layer disturbance, resulting in a nonlinear transition of the texture between the distinct HCP (002) and mixed HCP (110) and FCC (220) phases as the rotational speed increased (figure 5(c)). These results demonstrate the competing influences between the activation control originated from the nature of cathode materials and boundary layer disturbance resulted from the developed fluid shear.

Table 6. Results of XRD pattern analysis from strongly textured HCP (002) CoMnP films deposited with various agitation methods.

| Agitation of electrolyte   | Films on copper substrate | Films on CoP/Cu substrate |
|---------------------------|---------------------------|---------------------------|
|                           | 2θ (°)    | c (nm)     | FWHM (°) | 2θ (°)    | c (nm)     | FWHM (°) |
| 0 rpm                     | 44.745    | 0.40475    | 1.07594  | 44.742    | 0.40478    | 0.47273  |
| 0 rpm + air bubbling      | 44.698    | 0.40516    | 0.54405  | 44.700    | 0.40514    | 0.27637  |
| 15 rpm                    | 44.687    | 0.40525    | 0.42480  | 44.701    | 0.40513    | 0.26816  |

Figure 6. Hysteresis loops (normalized) showing the OP properties of CoMnP films on (a) copper and on (b) CoP/Cu substrates. The inset shows the second quadrant B-H curves according to the hysteresis loops.

Table 6. Results of XRD pattern analysis from strongly textured HCP (002) CoMnP films deposited with various agitation methods.
3.3. Magnetic properties

The MA of the Co HCP and FCC phases contributes to the out-of-plane (OP) and in-plane (IP) hard magnetic properties of Co-rich CoMnP films [33, 34]. XRD analysis revealed HCP (002) and FCC (111) peaks at 2θ = 44.762° (JCPDS No. 05-0727) and 44.216° (JCPDS No. 15-0806), respectively. No obvious FCC (111) peak appears in the XRD patterns in figure 4. The easy-axis of magnetization due to MA is the c-axis of the Co HCP lattice. Therefore, the textured HCP (002) Co crystallites led to significant OP hard magnetic properties. Figure 6 illustrates the representative OP hysteresis loops and the corresponding second quadrant of the magnetic induction (B) versus applied field (H) curves. For the CoMnP films on Cu substrates, the following optimal OP properties were obtained with a cathode rotational speed of 15 rpm: coercivity (Hc) of 1175 ± 7 Oe, remanence (Br) of 2270 ± 40 G, and energy product of 678 ± 3 kGOe. These properties are consistent with a previous report on electrodeposited CoMnP films [35].

With a heterogeneous mixture of HCP (110) and FCC (220) phases, the MA and planar shape anisotropy enhance the films’ IP hard magnetic properties. Figure 7 illustrates the representative IP hysteresis loops and corresponding second quadrant of the B-H curves. For the CoMnP films on Cu substrates, the following optimal IP properties were obtained with a cathode rotational speed of 60 rpm: Hc = 1040 ± 20 Oe, Br = 6690 ± 20 G and energy product of 1900 ± 20 kGOe. Because the compositions of the deposited CoMnP films were almost invariant for all deposition parameters (tables 3 and 4), the MA originated from the microstructural texture explains the optimal properties obtained for the OP and IP directions [36]. The VSM and XRD results of the CoMnP films deposited on the CoP/Cu substrates can also be explained through figures 4(b), 6(b), and 7(b). However, the optimal IP properties were exhibited by the films deposited at 120 rpm, rather than 60 rpm was the case with the Cu substrate, because high HCP (110) texture was obtained at different cathode rotational speeds on the CoP/Cu and Cu substrates (figures 5(a) and (b)).

The 0 rpm samples deposited without any electrolyte agitation presented unique IP properties (figure 7). The Hc, Br and energy product of the 0 rpm samples on the Cu substrates were 695 ± 7 Oe, 6200 ± 700 G, and 1100 ± 150 kGOe, respectively. The Hc, Br, and energy product of those on the CoP/Cu substrates were 740 ± 20 Oe, 4500 ± 1200 G and 1260 ± 160 kGOe, respectively. Considerable Br variation was noted after more than 10 replicates were measured. No obvious HCP (110) or FCC (220) peaks were observed in the XRD.
patterns of the 0 rpm samples (figures 4(a) and (b)), suggesting a different cause of these films’ IP properties. Surface roughness significantly affects the type, size, and movement of the domain wall [37, 38]. Electrodeposition with 0 rpm resulted in numerous crater-like micropits on the film surface. This rough surface contributed predominately to reducing the demagnetizing field in the IP direction. Furthermore, a considerable reduction of the grain size to the critical size of a few nanometers converted the Co crystallites from ferromagnetic to paramagnetic [8–11]. We used Lorentzian curve fitting to analyze the HCP (002) peak on the XRD patterns; the results are presented in table 6. The lattice constant of the c-axis, according to the JCPDS card, is 0.40461 nm. The 0 rpm films were less prone to expansion in the c-axis direction. According to Scherrer’s formula and the full width at half maximum (FWHM) [39], the calculated grain sizes of the 0 rpm films were 8–18 nm, and those deposited with electrolyte agitation were 16–32 nm. Generally, the electrodeposition with 0 rpm resulted in marginally lower Co and higher Mn content than did deposition with electrolyte agitation (tables 3–5). This additional Mn provided extra coupling effects and therefore the squareness of the hysteresis loops enhanced [6, 7]. The morphological features, grain size [40] and compositions of the 0 rpm samples illustrate their remarkable IP properties.

4. Conclusions

This study investigated the microstructural texture evolution caused by rotating-cathode electrodeposition of magnetic CoMnP thick films on various substrate materials. Identical CE and well-controlled mass transport limitation were realized for all electrodeposition in this study. With increasing cathode rotational speed, the microstructure transformed from a distinct HCP (002) texture to a completely heterogeneous mixture of HCP (110) and FCC (220) textures. In addition, the activation nature of the substrate material affects the relationship between the film microstructures and cathode rotational speed. The coupling of catalytic cathode materials and the boundary layer disturbance due to rotation induced fluid shear results in a nonlinear relationship between the microstructural texture and rotational speed. XRD and VSM results revealed the relationship among Co crystallographic texture, crystallite sizes, and MA. For CoMnP films electrodeposited via cathode rotation on Cu substrates, the following optimal OP magnetic properties were obtained at 15 rpm: Hc = 1175 Oe, and Br = 2270 G. The best IP properties were Hc = 1040 Oe, and Br = 6690 G, which were obtained at 60 rpm. This study’s results confirm the feasibility of rotating-cathode electrodeposition of hard magnetic thick films with tailored OP and IP properties.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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