Effect of electrolyte additives on structural and magnetic properties of cobalt ferrous tungsten phosphorous based thin films

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This work used urea as a cross - linking agent and phosphorous as precursors to electrodeposit crystalline Co-Fe-W-P thin films at a pH of around 8. To get the ideal soft magnetic characteristics needed for the next generation magnetic head core, electrodeposition conditions have to be altered. The formed films were characterised using SEM, EDAX, XRD, and VSM. The deposited films' SEM micrographs showed more homogeneous surface morphology and no micro-voids. X-ray diffraction patterns revealed that the films had an FCC phase structure. All of the coatings were nanocrystalline, as determined by calculating the average crystal size of the films using the debye Scherrer equation. The VSM findings showed that as grain size decreased, the coercivity of something like the nanocrystalline films drastically decreased. However, the chemical makeup of the films had a considerable impact on the magnetic moment, although grain size had little impact.

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1. Introduction

The production of the thin films may be done at a reasonable price via electrodeposition. It can be applied to composites, polymers, metals, and alloys. On a variety of substrates, it can also create coatings that call for faster deposition rates [1]. Due to its ability to create deposits for confined spaces, including the tiny pieces of machinery or other equipment, electrodeposition is also appropriate for any industrial application. By controlling the operational parameters, the characteristics of nanostructured material can be enhanced while its microstructure is regulated [2]. The need for nanoparticles with a broad spectrum of magnetic characteristics has been sparked by a variety of applications. Because of its capability, it is used for production of micro electromechanical systems (MEMS), researchers are becoming more interested in the investigation of the mechanical properties for lenient magnetic materials, like Cobalt based alloys, are frequently used magnetic materials in MEMS and NEMS [3-6]. Magnetic recording heads are where soft magnetic materials are most commonly used. Strong magnetic saturation, minimal coercivity, high porosity, almost no magnetostriction, excellent electrical resistance, and superior corrosion resistance are crucial requirements for elevated thin film recording heads [7].

Electroplated films are used in tiny sensors, actuators, and systems due to their minimum coercivity, relatively higher magnetic saturation, and superior corrosion resistance. Due to their potential usage in MEMS, the iron group metals (Ni, Co, and Fe) electroplated magnetic thin films have been created [8–10]. Among the most significant ferromagnetic elements in magnetic thin film materials is cobalt. Because it allows for the modification of deposit structure and, by extension, the magnetic characteristics of the deposits, electro deposition is also interesting for the fabrication of Co alloys. Materials with various structures, nanostructures, and magnetic characteristics can be produced dependent on preparation circumstances, like, the electrolyte

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composition, pressure, applied potential, the addition of additives. There have been reports on the impacts of bath compositions and impact of solution parameters, and electro deposition settings [11–13].

In the circumstance of magnetic recording devices, fine magnetic characteristics with appropriate mechanical features are necessary [14-16]. Despite having the greatest saturation magnetization, Co-Fe alloys has a strong coercivity and scientists used a variety of techniques to lower this characteristic [17–19]. Furthermore, the inclusion of a third element should be used to change these alloys' mechanical characteristics [20]. According to reports, the addition of tungsten to this binary alloy increases the alloys' hardness, abrasion resistance, durability, and heat resistance [21, 22].

Based on the mechanical, tribological, magnetic, and corrosion-resistant qualities of tungsten alloys, several investigations on deposition of tungsten (W) with Fe group metals have been conducted [16, 23, 24]. The non-metal element phosphorous (P) is doped into Fe-Co alloy films in order to develop their soft magnetic behaviour [25, 26]. This non-metal element can also strengthen electrical resistivity, oxidation resistance, and corrosion resistance. The electrodeposition of Fe-W [27], Ni-Fe-W-P [28], Co-W-P [29], and Fe-W-P [30, 10] films has also been the subject of various literary publications.

2. Experimental

2.1. Materials

In the electrodeposition process, a SS plate serves as the anode and a Cu substrate (1.5x5 cm) as the cathode. The current needed for electrodeposition was drawn from a DC-regulated power source. Chemicals of analytical grade have been employed to make the bath solution. Concentrated H_2SO_4 and acetone were used to clean the substrates. Prior to electrodeposition, these substrates were cleaned with distilled water and an alkaline electro-cleaning bath. Various concentrations of urea and phosphorous were used for the electrodeposition.

2.2. Method

An electrodeposition of a Co-Fe-W-P magnetic thin film was prepared using a solution comprising 0.1 M cobalt sulphate, 0.1 M ferrous sulphate, 0.05 M sodium tungstate, 0.3 M trisodium citrate, 0.16 M boric acid and 0.3 M ammonium sulphate (The aforesaid mixture was then combined with sodium hypophosphite solutions of 0.1 M and 0.2 M, additive urea of 2.5 and 5 gL^{-1} are added with 45 minutes of deposition time and three different current densities (2.5, 5, and 7.5 mA cm^{-2}) were used to investigate the produced thin films properties. The electrodeposition process was performed at a constant pH of 8.0.

2.3. Characterization techniques

The thickness of the deposition layers was measured using a digital micrometre made by Mitutoyo in Japan. A vibrating sample magnetometer was used to examine the magnetic properties of the deposited films. A scanning electron microscope (JEOL) and an X-ray diffractometer were used to study the magnetic films' crystalline structure and surface morphology (Rich Seifert, model 3000). The deposited Co-Fe-W-P film's crystallite size, stress, and dislocation density have all been determined using the XRD data. EDAX was used to determine how much Co, Fe, W, and P were present in the produced magnetic thin film. The hardness of the resulting thin sheet is assessed using a Vickers hardness tester (diamond indenter technique). The adherence of the films was then evaluated using the bend and scratch method.

3. Results and Discussion

3.1. Thickness Assessment

It is evident that the influence of the NaH_2PO_2 and urea concentrations on the thickness of the Co-Fe-W-P films produced under various conditions by adjusting the current density. The

thickness of the film grew with an increasing NaH_2PO_2 concentration both with and without urea. Significantly increasing current density and deposition time are accompanied by a rise in magnetic thickness on the substrate (Table 1). The Co-Fe-W-P deposition on the substrate significantly increases with longer deposition times. The increase in coercivity of the magnetic thin film and current density and deposition time also increases, as seen from Table 1.

3.2. Structural analysis

XRD analyses of electrodeposited Co-Fe-W-P films were performed. Another method for examining the nature and morphology of developed thin films is XRD. Cu Kα radiation with a wavelength of 1.54439 was employed. When the parameters from the XRD spectra well matched to the data from the JCPDS card number-65-7519, it was discovered that the data had cubic structure and predominately displayed the (210) plane. However, residual stress causes the plane peak in all XRD patterns to be slightly displaced. The stress of the material would cause the XRD peaks in the case of films and metals to move. A few peaks of modest intensity, such as (110) and (111) were also seen. Using the formula, the films' strain was determined from the peak of the XRD pattern.

$$strain\ (\varepsilon) = \frac{(\beta \cos \theta)}{4}$$

Table 2 shows that the Co-Fe-W-P film made from a solution comprising 2.5 g L^{-1} of urea has low stress, which was caused by homogeneous crystallographic orientation during electro-deposition. As a result, it should be highlighted how urea at lower concentrations refines grains and reduces stress. However, film stress also increases when urea concentration increases. This is a result of the additive's incorporation of degraded product whenever its concentration is higher in the film. The difference in lattice spacing causes the change in dislocation density, which changes the crystalline size [26].

$$Dislocation\ density\ (\delta) = \frac{1}{D^2}$$

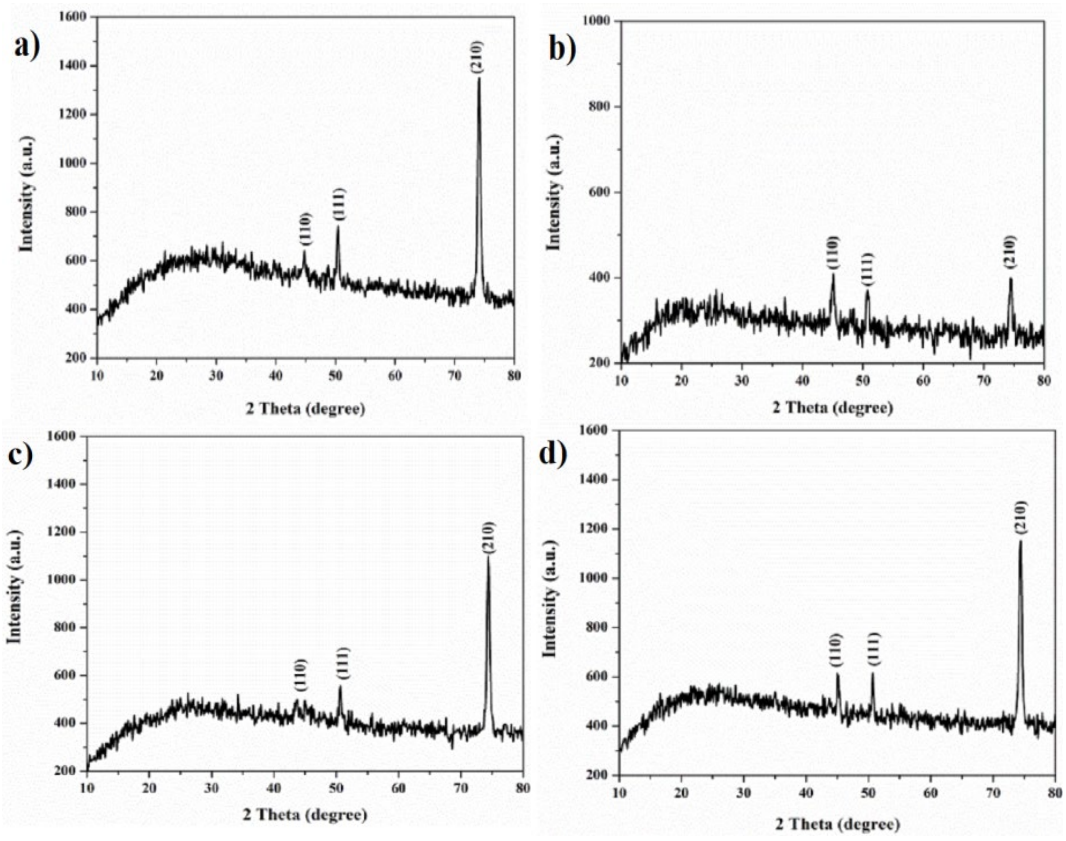

Fig. 1. XRD images of Co-Fe-W-P electrodeposited films.

When NaH_2PO_2 concentrations are increased by 0.1 M and 0.2 M with additive urea, the strain value rises from 13.711 x 10^{-4} to 32.769 x 10^{-4} and the dislocation density rises from 14.193 x $10^{14}/m^2$ to 81.074 x $10^{14}/m^2$, respectively. Table 2 provides the computed crystal size, strain value, and dislocation density of the Co-Fe-W-P alloy films. While the concentration of NaH_2PO_2 grows, the onset orientation of crystals causes the crystalline size of the deposition to decrease [31]. Using the Debye-Scherrer formula, the electrodeposited crystalline size was computed in the nano scale region.

$$Crystalline\ size = \frac{K\lambda}{\beta\cos\theta}$$

It was observed that when strain and dislocation density increase, the film's crystalline size decreases. The formation of additional dislocations causes the dislocation density to increase in deposited film. The barrier to future dislocation motion steadily rises as a result of the expansion and overlapping of the strain regions of nearby dislocations. As a result, the metal becomes harder as the distortion develops.

3.3. Elemental Analysis

An EDAX analysis used to perform an elemental analysis on magnetic thin films. Table 2 displays the weight percentages of Co, Fe, W, and P. According to the findings, the thin film was created has a high content of cobalt and iron even without the addition of urea. All of the films produced using different baths were found to have low phosphorous content. The films had strong magnetic characteristics despite having little phosphorous in them. The bath's urea addition is what made the Co-Fe-W-P films crystalline structure better.

3.4. Morphological observation

The SEM view of electrodeposited Co-Fe-W-P thin films at different 7.5mA cm^{-2} current densities of NaH_2PO_2 (a), 2.5 (b) 5 g L^{-1} urea with 0.1 M of NaH_2PO_2 (c), 2.5 (d) 5 g L^{-1} urea with 0.2 M of $NaH_2PO_2.2H_2O$, are shown in Figures 2 (a – d). The crack-free and homogenous shape of thin films is clearly demonstrated by the SEM imaging. Bright and evenly covered on the surface, the thin films are. They seem flawless, with no cracks.

Table 1. The thickness and magnetic properties of the prepared Co-Fe-W-P thin films.

Bath additive		Current density ($mAcm^2$)	Thickness of film (μm)	Magnetic saturation (emu)	Remanent polarization (emu)	Coercivity (Oe)	Squareness
Phosphorous (M)	Urea (g/l)						
0.1	0	2.5	2.6	0.151	0.054	166.08	0.35
		5	2.73	0.194	0.056	139.66	0.28
		7.5	3.5	0.104	0.006	124.62	0.05
	2.5	2.5	3.5	0.04	0.012	176.02	0.3
		5	3.8	0.033	0.006	123.81	0.18
		7.5	4	0.1	0.018	119.18	0.18
	5	2.5	3.8	0.074	0.026	170.51	0.35
		5	4.1	0.123	0.034	151.49	0.276
		7.5	4.4	0.09	0.02	133.87	0.222
0.2	0	2.5	3.57	0.073	0.018	129.84	0.24
		5	3.33	0.063	0.013	108.43	0.2
		7.5	3.67	0.103	0.014	140.79	0.135
	2.5	2.5	3.9	0.059	0.021	187.39	0.355
		5	4.2	0.077	0.020	149.81	0.25
		7.5	4.6	0.131	0.030	136.3	0.22
	5	2.5	4.1	0.061	0.017	160.3	0.27
		5	4.5	0.079	0.018	157.40	0.22
		7.5	4.8	0.077	0.018	151.38	0.23

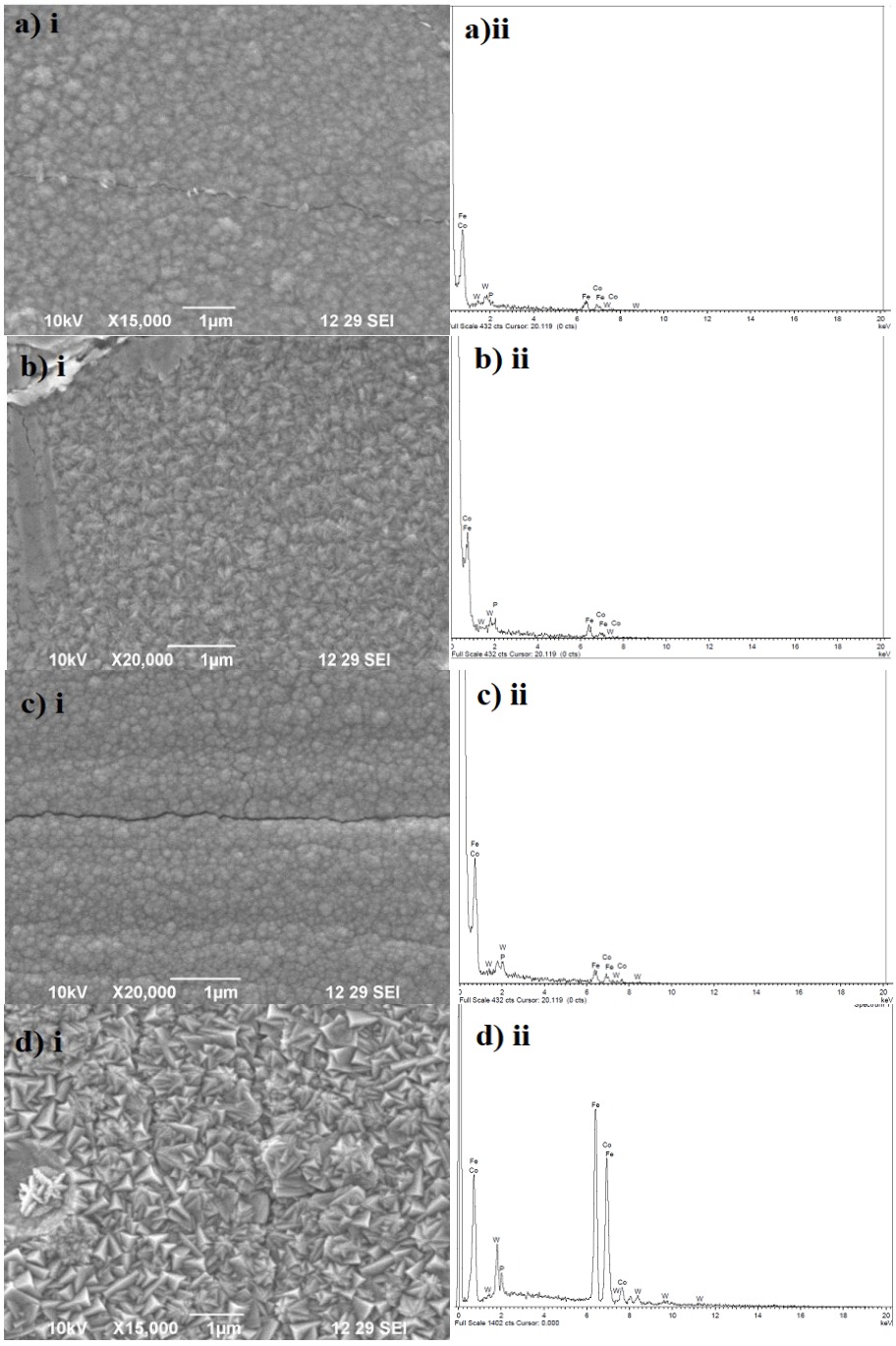

Fig. 2 SEM images and EDAX spectra of Co-Fe-W-P electrodeposited films.

3.5. Mechanical Properties

Vickers hardness testers were used to test Co-Fe-W-P coated thin films to determine the hardness and their calculated values are shown in Table 2. Vickers hardness tester was used to measure the micro hardness of the deposits. The prepared thin films have hardness values of 158, 159, 163, 165, 166, and 168 VHN. Therefore, hardness testing reveals that increasing the bath concentration with additive urea enhances micro hardness because there is less stress associated with thin coatings. To ensure that the film had adequate adhesion, bend testing and scratch testing were conducted.

3.6. Magnetic Studies

Co-Fe-W-P electrodeposited thin films, VSM images were depicted in Figures 3(a), 3(b), 3(c), and 3(d). The electrodeposited film, however, has comparatively strong magnetic characteristics. The maximum coercive and remanent polarizations, for instance, were determined to be 124.62 Oe and 0.006 emu in the absence of urea. The addition of NaH_2PO_2 was found to generally have minimal impact on the film thickness. The coercivity was observed to rise from 124.62 Oe to 140.79 Oe while the concentration of NaH_2PO_2 was increased from 0.1 to 0.2 M. However, it was discovered that the film's morphology was excellent when there was no urea added to the electrodeposition solution.

Investigations were conducted to determine the impact of adding urea and NaH_2PO_2 to the bath. The deposit's properties and magnetic properties greatly enhanced with the addition of modest concentrations of urea. The ideal conditions demanded for the addition of 2.5 g L^{-1} of urea, 0.1 M of NaH_2PO_2, and a current density of 7.5 mA cm^{-2}. The film was also reported to be 4.0 m thick with coercive and remanent values of 119.18 Oe and 0.018 emu, respectively. With each subsequent increase in urea concentration, it was shown that the thickness, coercive, as well as remanent values drastically increased.

Urea is primarily responsible for the films improved magnetic characteristics. Thus, it is discovered that the urea molecules have a levelling effect, ensuring that crystals during electrodeposition are oriented uniformly. The magnetic characteristics of the films increased at random when the levels of NaH_2PO_2 and urea increased. The film particle size was significantly increased and its corrosion behaviour was decreased as a result of the addition of the phosphorous-containing additive urea.

Table 2. Crystallite size, strain, dislocation density, hardness and composition of Co-Fe-W-P thin films at 7.5 mA cm^{-2} current density for 45 minutes deposition time.

Phosphorous (M)	Urea (g/l)	Crystallite size (nm)	Strain 10^{-4}	Dislocation Density (10^{14} / m^2)	Vickers Hardness Number (VHN)	Film Composition (wt%)			
						Co	Fe	W	P
0.1	0	26.54	13.711	14.193	158	41.76	49.95	4.05	4.24
	2.5	20.49	17.756	23.804	159	36.09	50.3	7.15	6.46
	5	14.79	24.607	45.715	163	13.46	44.37	9.97	32.20
0.2	0	23.90	15.223	17.496	165	43.19	47.08	4.45	5.28
	2.5	16.61	21.911	36.246	166	27.27	31.59	9.64	31.50
	5	11.10	32.769	81.074	168	15.64	31.05	31.03	22.28

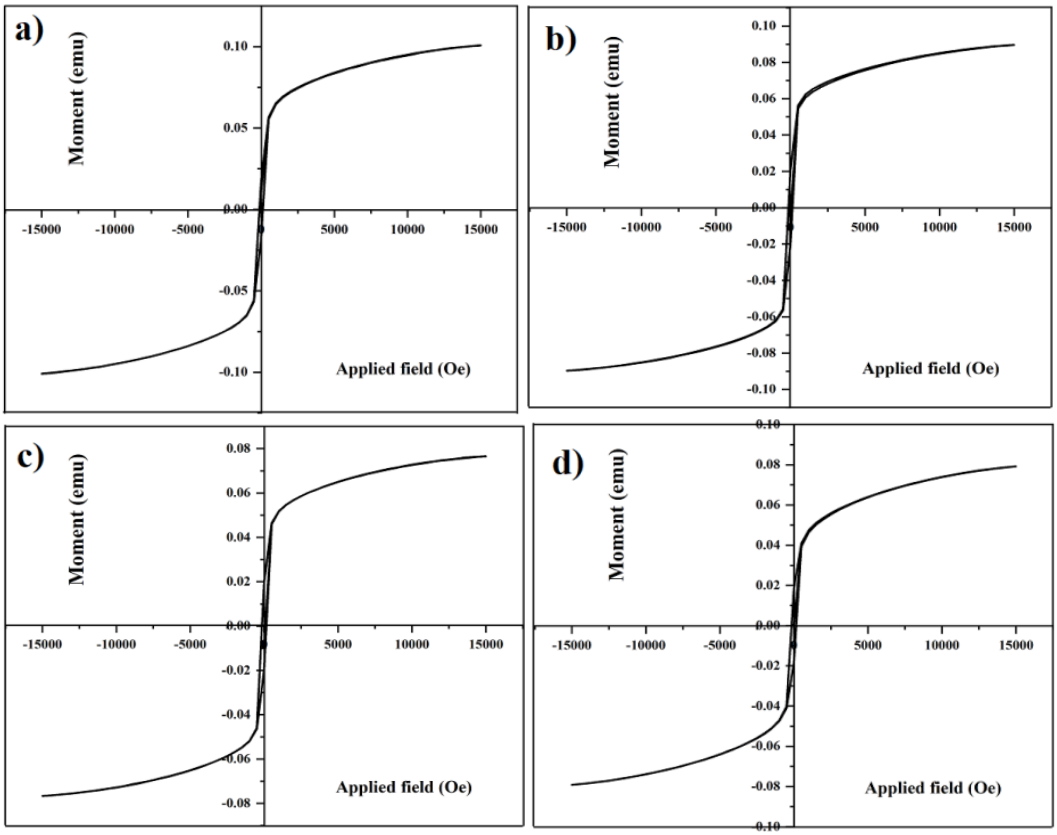

Fig. 3 shows VSM images of electrodeposited Co-Fe-W-P films.

Generally, current density increase led to an increase in film thickness and magnetic characteristics (coercivity and remanence). While increase in current density, the films magnetic concentration level also increased at random. The coercivity of the films formed from a bath containing 2.5 gL^{-1} of urea increased when compared to the films formed from 0.1 M and 0.2 M of NaH_2PO_2. Additionally, there is an increase in coercivity (in 5 gL^{-1} of urea) when NaH_2PO_2concentration is increased from 0.1 M to 0.2 M. As the concentration of NaH_2PO_2 is increased with the addition of urea, it is evident from Table 1 that the decrease in coercivity of the magnetic thin film [32, 33].

4. Conclusion

By electrodeposition, a Co-Fe-W-P thin film with varying NaH_2PO_2 and additive urea concentrations was created. The additional benefits of thin film technology are confirmed by bright and evenly coated thin films. The produced thin film has a cubic crystal structure, according to the XRD data. While increasing the concentration of NaH_2PO_2 with additive urea, the crystalline size reduces because of the beginning orientation of crystal. This is a result of deposits nanocrystalline structure. Co-Fe-W-P has good strong magnetic characteristics. The purpose of this experiment was to examine the magnetic characteristics of nanostructured Co-Fe-W-P films.

It was observed that doping urea with lower concentrations achieved higher magnetic features with strong coercivity. This is due to the finding that the urea molecules have a leveling effect that assures consistent crystal orientation during electrodeposition. The coercivity of the films is dramatically reduced when the urea concentration is raised. The rise in urea concentration causes the films to become harder. These magnetic films should be under the minimal amount of stress possible because they are employed in MEMS devices. The bath's optimum urea content

was determined to be 2.5 g L^{-1} in order to produce film with better morphology, magnetic, and mechanical characteristics.

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