

Aging Effects of Electroless Cobalt Bath On Microstructure & Magnetic Properties of Co-P Films

By E.E. Kalu

The performance properties of electroless Co-P alloy may vary considerably with respect to the time of bath usage. This paper describes such bath aging effects on the microstructure and magnetic properties of Co-P thin films. When the bath is highly active (young age), a deposit made up of interconnected grains with high phosphorus content is produced. As the bath ages, the average size and shape of the deposited grain and the level of the film's phosphorus content decrease. The changes in sample microstructure result in decreased magnetic coercivity. A thermal treatment was shown to rejuvenate the inactive bath, suggesting that a cobalt complex is responsible for the loss in activity.

The dramatic increase in the storage capacity of magnetic memory discs has been made possible by the replacement of particulate media with thin magnetic alloy films. Although these thin films can be deposited by many methods, sputtering has recently become the preferred method for many applications. Electroless deposition, however, is known to provide superior functional, thin magnetic-alloy films for some applications. An example in which electroless deposition is preferred is the incorporation of magnetic thin films into a document (*e.g.*, currency) as a security measure for detecting counterfeits. For such applications, sputtering cannot be used because both the magnetic properties and aesthetic qualities required cannot be met by this method. Particulate magnetic media cannot be used because they do not meet the aesthetic requirements of such documents.

The application of deposited magnetic thin films for security purposes requires deposits of uniform and invariant physico-chemical properties and a semi-batch plating process. The composition of plating solutions and the plating process variables are known to control the composition and properties of electroless magnetic alloys.¹ The significant variables in the deposition process include substrate treatment prior to plating, mass transport conditions, temperature, variation in the concentration of the active species in the plating bath and the plating solution pH. It is known, however, that many of the deposit properties, including magnetic properties and alloy composition, depend on these plating variables. The relationship between the deposition parameters and the deposited film properties is not well understood despite a large number of studies conducted by many investigators. Consequently, a significant batch-to-batch variation can result in magnetic property variations in the plated films. Not only is this true for an electroless cobalt bath, but in addition, magnetic properties of the deposited Co-P alloy film can vary as a consequence of the length of time the bath has been in use. The variation is attributed to the formation of inactive cobalt species that affect the nucleation process.

The age of a bath is measured from the time all conditions required for plating have been met. The nucleation

or deposition rate of electroless Co-P alloy varies with the age of the bath. The nucleation rate was found to be important in determining the microstructure of deposited Co-P thin films.²⁻⁴ Mirzamaani *et al.*,³ keeping plating parameters constant, considered the effect of nucleation (through substrate treatment) on the magnetic properties of deposited film. Under constant plating conditions, they showed that high magnetic properties are associated with shape and strain anisotropies of the Co-P crystallites, suggesting that the magnetic properties are highly dependent on the substrate treatment. Unfortunately, these results were obtained in freshly prepared solutions and precluded the effect of bath age on the films. Change in plating rate affects the microstructure of the deposited film and its consequent magnetic properties. The loss in bath activity, attributable to the presence of oxygen, hinders the development of a semi-batch electroless cobalt process. In the presence of oxygen and a favorable pH, cobalt forms hard-to-reduce (by the reducing agent) complexes. The complex formed by air oxidation of a Co(II) salt was identified as a Co(III) complex by Alberts *et al.*⁵ Cobalt(III) complexes are probably un-reactive relative to the reducing agents used for the electroless plating. Spectrophotometric analysis of cobalt bath solutions in the absence of oxygen showed that the bath solutions contain only Co(II) salt complexes.⁶⁻⁸

Bath Life Extension

Despite the well known short life span of ammoniacal-cobalt baths, there is little information in the literature on how to extend the life of an electroless cobalt bath for continuous plating. Recently, Honma and Noguchi⁹ used chemical additives to combat the oxygen effects and extend the life of an electroless cobalt bath. They extended a tartrate-ammonia cobalt bath from two days to more than 10 by adding diamine borane or hydrazine sulfate. Matsuda and Takano⁶ discussed the effect of dissolved oxygen on the nucleation rate of cobalt. They were not able to reverse the deteriorated

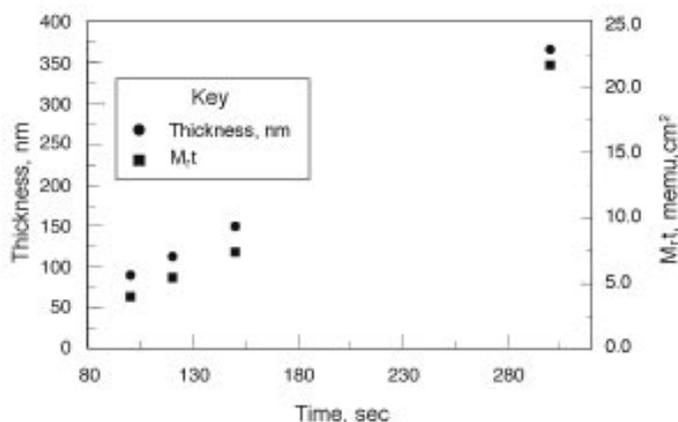


Fig. 1—Dependence of M_t and thickness on plating time.

plating rate; however, with a continuous nitrogen gas charge, they were able to prevent the aging process. Their conclusion was that dissolved oxygen affects primarily the cobalt nucleation rate and, consequently, affects the growth rate only slightly. If this hypothesis is true, then irrespective of the age of a bath, the deposited films (for lengths of time longer than the nucleation period) should all possess similar microstructural features.

There has not been any study on the effects of bath aging on the microstructure of cobalt deposits. The study and understanding of the grain-to-grain interactions in magnetic thin film media is important because these interactions control the magnetic properties of the media. This paper reports on a study of the influence of bath aging on the microstructure of magnetic thin films and how this knowledge could be used to modify or optimize the process conditions. Because nucleation is influenced to a great extent by the substrate and, to a lesser extent by plating parameters, an investigation of the effect of plating parameters on the deposited thin film requires substrates with uniform conditions. A unique catalyzation method that keeps the substrate surface uniform was used. Remanent magnetization is an important property of the films studied. The significance of this study is that it provides a basis for understanding the intergranular interaction changes that result from aging of a cobalt bath. The results will provide insight on how to design a continuous or semi-batch electroless plating process for cobalt.

Experimental Procedure

Thin films of electroless Co-P alloy were deposited on catalyzed polyethylene terephthalate (PET) films at the same resident or immersion times (2 min), but at different bath ages. The treated PET substrate was catalyzed by the application of a thin film coating containing a palladium salt. The catalyst coating or ink, in addition to the palladium salt, contains a carrier polymer binder. A typical catalyst ink formulation is composed of (wt pct) 4.9 percent polyvinyl butyral, 1.25 percent palladium (added as palladium acetate trimer) and the balance acetone. The palladium acetate was dissolved in a 10-mL acetone solution to obtain solution A. Polyvinyl butyral was then dissolved in the balance of the acetone to form solution B. Solutions A and B were then mixed with stirring to form the catalyst ink.

Depending on the method of application, other viscosity modifiers and adhesion promoters could be added in the ink. The prepared ink was printed on 480 anilox roll on treated PET films to obtain 3/4-in. stripes. The printing method al-

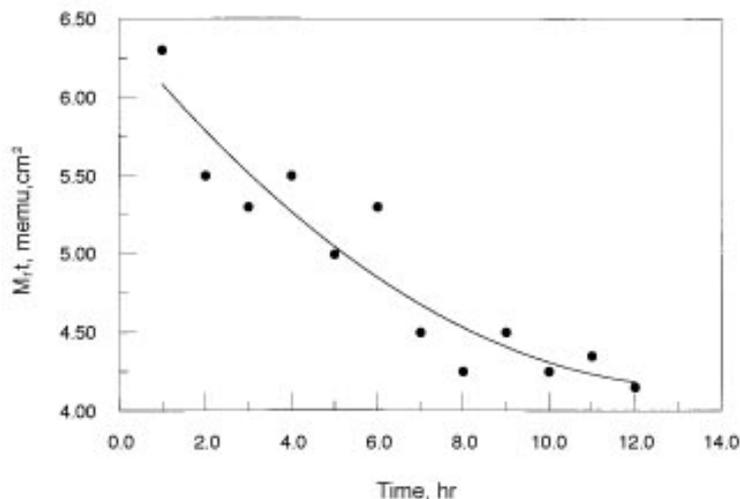


Fig. 2—Variation of remanence-thickness product with bath usage.

lowed a uniform (in thickness) catalyst to be laid on the PET. Following the application, the catalyst coating was dried at 100 °C and activated thermally. The activation temperature was between 160 and 200 °C for time periods between 10 and 30 min. This catalyzation method does not use colloidal tin solution for activation, nor generate as much waste as the traditional method. The bath was based on a cobalt amino-tartrate complex with cobalt sulfamate as the source of Co⁺² ions (5.0 g/L), sodium tartrate (100 g/L) as the complexing agent for Co⁺² ions in the bulk solution, borax or boric acid, H₃BO₃ (30 g/L) as the buffer, sodium hypophosphite, NaH₂PO₂ (20 g/L) as the reducing agent and glycine (10 g/L) as a complexing agent for Co⁺² ions in the diffusion layer. The bath operating temperature was 65 °C and the pH (9.5) was adjusted with KOH. Cobalt was analyzed by the atomic absorption (AA) method, while hypophosphite was analyzed by addition of potassium iodide (KI) and back titration of iodide. For the sodium tartrate and glycine complexers, their composition was determined by Dionex. An X-ray diffractometer (Cu K α) was used to measure the structure and texture of the magnetic layer and the underlying films. TEM analysis was used to characterize the samples. Morphology was investigated by SEM and composition was determined by microprobe elemental analysis. Film thickness was measured by XRF and a vibrating sample magnetometer (VSM) was used to measure the magnetic properties.

Results & Discussion

The dependence of the thickness and remanence-thickness product of the plated film on the immersion or plating time

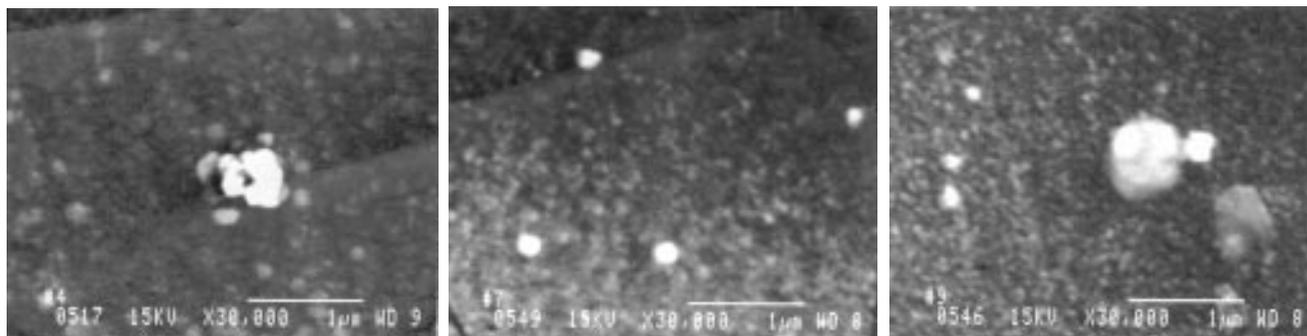


Fig. 3—SEM micrographs of Co-P thin films deposited at different bath ages.

for a freshly prepared bath is shown in Fig. 1. Both the thickness and remanence-thickness product increased linearly with the time of immersion for a freshly prepared solution. This suggests that the PET substrate is uniformly catalyzed and, as a result, the nucleation rate for the magnetic deposit is uniform on the substrate. Moreover, the time required for a specified thickness or remanence-thickness product could be estimated from the figure. For the present study, interest was on the remanent magnetization-thickness product ($M_r t$).

Magnetic thin films used for security applications must possess high remanent magnetization-thickness product ($M_r t$). Figure 2 shows the variation in the remanence-thickness product of a film as a function of bath age. The operating conditions, including the immersion time (2 min) for the plated films, were constant during the run of Fig. 2. Deionized water was added to make up for the loss of evaporated water. Make-up active chemicals (cobalt, hypophosphite, etc.) were also used. Accordingly, the only variable is the age of the bath used for plating. The figure shows that $M_r t$ decreases with bath age. Matsuda and Takano reported that oxygen or bath aging strongly affected the nucleation rate;⁶ however, because $M_r t$ depends strongly on the microstructure of the deposit, the result shown in Fig. 2 suggests that oxygen or bath aging also has a very strong effect on the microstructure of the deposit.

To test this hypothesis, in another set of experiments, three samples, labeled A, B and C, were plated at bath ages of 0, 8 and 24 hr, respectively. A cross section of the samples observed by TEM showed two distinct layers—a grain layer (most probably the catalyst layer) and a crystalline columnar growth. The grain layer consists of small but numerous grains. The top layer of the film (above the catalyst layer) consists of large grains coalesced from many grains. The sizes of the individual columnar crystalline structures show that sample A > B > C. This was also the order of the coercivities. SEM micrographs (Fig. 3) of the three samples studied

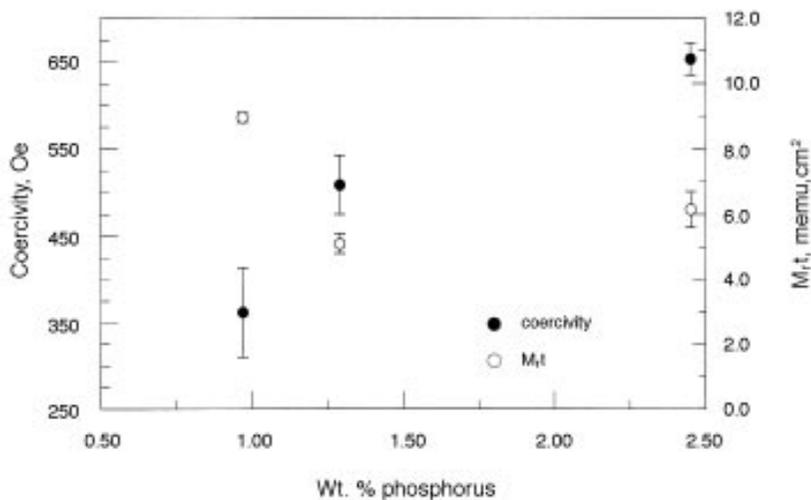


Fig. 4—Magnetic properties of thin Co-P film as a function of wt pct phosphorus.

showed differences in the grain size and grain definition or perfection. Here, grain definition or perfection is used to define the shape of the grains. From these results, we can distinguish the following structures; whereas sample A has both large and well-defined grains (slightly elongated), the average grain size of sample B is smaller and less well defined. Sample C has the least average grains in both size and perfection. At high magnification, however, the uniformity of the plated film follows an opposite trend: C > B > A. X-ray diffraction spectra obtained for the three samples shows hcp cobalt phase with three peaks identified as (101), (100) and (002). No major Co lines were favored in any of the samples. The strongest peak is the (101) peak. The observed peaks suggest a polycrystalline deposit.

Elemental analysis of the three samples showed that (i) phosphorus level was not constant (2.45, 1.29 and 0.97 wt pct for samples A, B and C, respectively); (ii) palladium wt pct (within the sampled volume) was not constant and decreased as the amount of phosphorus in the film increased (0.82, 1.29 and 1.57 wt pct for A, B and C, respectively). The coercivities and remanent-thickness products of these samples are plotted against the phosphorus content as shown

in Fig. 4. Whereas the coercivity of the film increases monotonically for phosphorus content between 0.5 and 2.5 wt pct, the remanent thickness does not. It is well known that the origin of high coercivity in the Co-P film is attributed to the size, separation and perfection of the grains. Grain size, grain definition and grain separation are the dominant factors in determining the

Table 1
Comparison of Three Samples of Co-P Alloy Film
Plated at Different Bath Ages

Sample A	Sample B	Sample C
Interconnected grains	Similar to A; smaller grains	Very small grains; appear discrete
Very few voids	Between A & C	Uniform coverage
162 nm avg grain size	102 nm avg grain size	99 nm grain size
Numerous nucleation sites	Same as A	Same as A
Co(101), (100), (002)	Co(101), (100), (002)	—
2.45 wt pct P	1.29 wt pct P	0.97 wt pct P
635 Oe	475 Oe	310 Oe
8.8 memu/cm ²	4.8 memu/cm ²	5.6 memu/cm ²
SR* = 0.67	SR = 0.55	SR = 0.70

* Squareness Ratio

Table 2
Effect of Heat Treatment on Electroless Co Bath
pH 9.0

Time hr	H _c Oe	M _t memu/cm ²	Temp °C	Comments
0	238	5.22	65	No heat treatment
12	293	4.34	65	No heat treatment
24	300	4.06	65	No heat treatment
24	460	6.18	80	80 °C for 90 min

value of the coercivity. Phosphorus in the film increases the interparticle separation, resulting in a lower interparticle interaction. As the interparticle separation increases (decreasing interparticle interaction), the coercivity increases. This explains the observed trend in Fig. 4 for the coercivities and the results agree with the observation of Chen *et al.*² Further, the observed grain definitions strongly correlate with the coercivities of the samples, and the results agree with the observation of Mirzamaani *et al.*,³ who showed that grain shape or definition (not size) affects coercivity. The remanent-thickness product and wt pct P relationship, as observed in Fig. 4, suggests that a minimum value for M_t exists near 1.25 wt pct P. The origin of such a minimum is neither known nor understood. Because the bath operating conditions and the initial nucleation were constant, it can only be concluded that bath aging strongly affects Co-P film magnetic properties. This effect results from changes in film composition and microstructure, induced by the aging process.

Bath Rejuvenation or Treatment

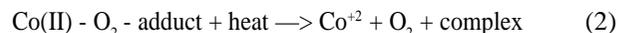
The major characteristics of samples A, B and C are summarized in Table 1. These results suggest that the plating rate or the activity of the bath decreases with age. The decrease in the bath activity is known to result from gas (oxygen) saturation that influences some hydrolytic phenomena in the bath. This decrease in bath activity results in the lowering of phosphorus that is included in the plated film alloy and affects the grain definition as well. To maintain physico-chemical properties for the plated film, bath activity must be maintained at a fixed level. Recently, Honma and Noguchi⁹ extended a tartrate-ammonia cobalt bath from two days to more than 10 days by adding diamine borane or hydrazine sulfate. The additives were credited with restraining the formation of difficult-to-reduce cobalt complex species. For instance, dimethylamine borane extended the bath life by accelerating oxidation reactions. The role of the chemical additive (*e.g.*, dimethylamine borane, DMAB) can be represented as follows:



Non-agitation of the bath during many of the experiments by Honma and Noguchi⁹ should be noted. Agitation of the bath is known to increase the amount of dissolved oxygen, which favors the formation of difficult-to-reduce cobalt complexes. A documented example of the effects of agitation on bath chemistry is provided in the work of Dragieva-Miladinova *et al.*,¹⁰ on Ni-Fe film. They show that agitation influences the morphology, structure and magnetic proper-

ties of Ni-Fe deposited on mylar film. They observed that magnetic films obtained with agitation are built up from smaller-sized grains, have higher coercive force and exhibit oriented structure at greater thickness. Although they obtained high coercivities with smaller-sized grains, no mention was made of grain definition.

Based on these results, agitation was not recommended for the formation of Ni-Fe magnetic films. The problem with the chemical treatment approach outlined above is that the added foreign chemical species could be incorporated into the alloy films, thereby changing the magnetic characteristics of the films. An alternative approach that was employed in our laboratory was the subjection of the inactive bath to a temperature higher (80-90 °C) than the bath's operating temperature (65 °C) for a duration of 45 min or more. After cooling the bath to its operating temperature, it was found to be rejuvenated. Table 2 summarizes a typical result of the thermal treatment. In a semi-batch process, the bath was recirculated through a heat exchanger at which the recycled solution was heated to a high temperature of 80 °C. This approach resulted in a substantial uniform plating during a long operation of the bath. The low temperature (80-90 °C) at which the cobalt complex formed was decomposed, suggests that a Co(II)-O₂ adduct (instead of a Co(III) complex) is responsible for bath inactivity with aging. The reaction occurring during the thermal treatment is therefore thought to involve the decomposition of a Co(II)-O₂ adduct as follows:



Equation (2) is speculative because the identity of a cobalt complex that can be thermally decomposed at 80-90 °C, or chemically decomposed, is not yet known and for which no spectral test was made.

Conclusions

Results show that as an electroless cobalt bath ages, the interconnectedness of the deposited grains changes. When the bath is highly active, the deposit is made up of coarsely interconnected grains with phosphorus at the boundaries. This structure favors a high magnetic remanence-thickness product. On the other hand, as the bath ages, more uniform deposits occur. This does not lend itself to greater inclusion of phosphorus, resulting in a film of low remanence-thickness product. Although thickness is important in the characterization of a film's magnetic remanent-thickness product, M_t, results indicate that coarse grains with high phosphorus content may be more important. Thermal treatment may be an effective method of keeping a cobalt bath active for continuous electroless cobalt plating.

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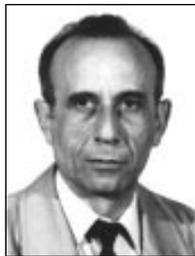
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continued from page 73

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