Sputter Seeded Nucleation of Smooth Electroless Nickel Growth

by Leonard Nanis[*]

A combined sputter-plate method has been developed which uses a sputtered thin seed layer to initiate autocatalytic deposition of smooth electroless nickel (Ni-P).[1,2] The final plated Ni-P surface is free of nodular growth and conforms to the initial smoothness of the substrate. Sputtering of the thin sputtered catalyst layer completely replaces conventional surface preparation such as the zincating of aluminum. The seed-plate method may also replace conventional treatments which etch surfaces during oxide removal from other metals prior to Ni-P plating. Freshly sputtered Ni-P seed layers remain active and nucleate Ni-P deposition even after wait times of 24 hours or longer before plating.

Electroless nickel plating on aluminum alloys is a widely practiced process which plays a key role in the manufacture of rigid magnetic memory disks. Mechanical damage to the soft aluminum is prevented by the harder Ni-P surface layer, generally "hi-phos" 12 wt% P. The aluminum alloy surface is conventionally activated prior to Ni-P plating by a series of chemical etch solutions followed by double zincating, as reviewed by Hajdu.[3]

For aluminum memory disk substrates, the thickness of the as-plated Ni-P layer is typically about 13 μm (~500 μ-in.). Any nodular growth which contributes to the roughness of as-plated Ni-P is then removed in two or more polishing operations so as to provide a smooth surface for the addition of the magnetic layer. The several steps involved in surface preparation and production of finished rigid memory disks are reviewed briefly by Duffek, *et al*.[4] Additional details are described elsewhere.[1,2]

Nodular Ni-P growth on conventionally zincated aluminum alloys may be related to intermetallic particles in the aluminum alloy matrix. Surface roughness of the Ni-P may also be related to non-uniform etching of surface or subsurface regions of residual cold work on machined, ground or polished substrates when immersed in strongly alkaline zincate solutions.

Steady improvement in the cleanliness of Al-4.5 wt% Mg alloys has reduced the influence of intermetallic particulate inclusions on the formation of nodular Ni-P. Typical intermetallics are silicides and aluminides, formed by reaction of liquid matrix Al and Mg with trace amounts of iron, silicon and manganese impurities.

Mechanical methods to obtain flat and smooth initial surfaces of aluminum substrates have included lathe-turning with diamond tool-bits and grinding. Efforts to grow smooth Ni-P on pre-polished smooth aluminum alloy using conventional zincating have been unsuccessful, yielding patchy Ni-P deposits having non-uniform patterns of nodule growth. Little has been reported about the cause of such patterned nodule deposition, but it may be linked to non-uniform etching during zincating. Regions of substrate surface and sub-surface cold work may play a role similar to etching effects attributed to cold-work or so-called Beilby layer effects encountered with surfaces polished for metallography.[5,6]

Nuts & Bolts: What This Paper Means to You

Electroless nickel plating on aluminum alloys is key to the manufacture of rigid magnetic memory disks. Recent order of magnitude increases in memory storage capacity have brought new requirements for the smoothness of the final surface. Average roughness (R_a) values of 2 to 5 Å are common. Newer materials such as highly polished glass and glass-ceramic with R_a values below 1 Å now offer competition. This paper introduces a new approach for aluminum, where a sputtered thin seed layer of Ni-P is deposited to allow the deposition of smooth electroless nickel, completely replacing conventional zincating. The results are upbeat, in terms of performance as well as cost.

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In general, a loss of aluminum in the first zincating step is expected. From measurements of mass change in the zincating process, Azumi, *et al.*[7] verified an aluminum mass loss close to 27% of zinc mass gain.

A mass loss ratio of Al / Zn = 0.275 (absolute values) fits the requirement of the following displacement reaction:

$$3Zn(OH)_4^{-2} + 2Al \rightarrow 3Zn + 2Al(OH)_4^- + 4(OH)^-$$

However, the growth of Zn in the first zincate step is highly localized at active sites.[8] Similarly, non-uniform localized dissolution of Al is to be expected, with an associated roughening of the initial surface.

The present seed-plate method completely avoids non-uniform etching which might occur at any stage of conventional surface preparation. The sputtered binder and seed layers mask chemical and electrochemical effects due either to the presence of intermetallic particulate phases or to non-uniform etching of residual cold-worked regions in the aluminum alloy surface.

Recent order of magnitude increases in memory storage capacity have brought new requirements for the smoothness of plated and polished electroless Ni-P on aluminum substrate surfaces. Average roughness (R_a) values of 2 to 5 Å for polished Ni-P are common. Newer substrate materials such as highly polished glass and glass-ceramic with R_a values of less than 1 Å now offer competition to Ni-P plated and polished aluminum alloys.

A good low-cost substrate should preferably have low density combined with high strength in order to resist centrifugal stresses and vibrational deflections induced by high speed disk rotation. A key requirement is also that the substrate material be non-magnetic.

Seed-plate sputter materials

For the seed-plate method applied to magnetic disk substrates, the sputtered catalytic seed layer should be non-magnetic and also form a good bond with the nucleated Ni-P. There are several non-magnetic nickel-base alloys suitable as seed layers which are also commercially available as sputter targets.

Nickel-phosphorus alloy is well-suited as a seed layer by definition since, once initiated, Ni-P normally functions as a continuously renewed autocatalytic seed surface. Nickel-phosphorus sputter targets are also presently commercially available.

Following the introduction of the seed-plate concept for memory disk substrates,[1] the method has been amply verified by other investigators. Closely related studies have been made for aluminum alloy,[9] glass and glass-ceramic substrates.[10,11]

To promote adhesion between the seed layer and the substrate, the seed-plate method first introduces a thin sputtered underlayer of chromium. For example, a 300-Å chromium first layer binds the aluminum alloy substrate to a 300-Å sputtered Ni-P seed layer which, in the Ni-P plating tank, nucleates electroless Ni-P growth. Good adhesion is obtained even in the maximum stress region of a drastic bend test where the plated substrate is folded and bent nearly 180° [Fig. 1(a)]. From a practical viewpoint, both binder and seed layer should be as thin as possible in order to maximize sputter system throughput.

Experimental

Thin sputtered layers were added to memory disk substrates of type 5586 aluminum-4.5% Mg alloy (100 mm OD, 36 mm ID) in a standard 13.56 megahertz radio-frequency sputtering system.** Substrates received no special cleaning before loading into the sputtering system. Nickel-phosphorus with 11 to 12 wt% P was plated onto as-sputtered substrates suspended without rotation in a commercial bath*** operated at 85 to 90°C (185 to 194°F).

The sputtering system was outfitted with 20.3-cm (8-in.) diameter targets of chromium and Ni-P. The Ni-P sputter target was prepared by electroless deposition directly onto a standard 20.3-cm (8-in.) diameter copper backing plate. The sputtering system provided single-sided sputtering with targets positioned above a horizontal workpiece. Accordingly, each side of the substrate was coated in separate sputter operations. As mentioned, a layer of chromium was first sputtered to promote adhesion.

Optical non-contact surface profiles served as an overall quantitative measure of surface roughness. The surface finish of the aluminum substrates before and after seed-plate treatment was determined with a Doppler laser vibrometry non-contact profilometer**** which scanned the entire surface of the substrate. Plated Ni-P thickness was determined by X-ray fluorescence.†

Separately, seed-plate experiments were also made with a totally different type of sputter system that provides high-rate simultaneous two-sided deposition. Aluminum alloy 5586 substrates were coated with binder and seed layers in a DC magnetron system,†† widely used in the disk industry for sputter deposition of magnetic layers. Sputter-seeded substrates were simultaneously Ni-P plated with conventionally zincated substrates, which provided a control group for comparison.

Seed-plate substrates were sputter-coated first with a 300-Å chromium binder layer followed by a 300-Å sputtered Ni-P seed layer (20 at% P). After vacuum sputtering, the substrates were stored and held in reserve until they were immersed in the Ni-P tank at the final station of a production tank line along with conventionally zincated substrates. For simultaneous plating of both zincated control and sputter-seeded substrates, a multi-carrier mandrel array of control substrates was activated routinely in the various chemical and rinsing stations for conventional double zincating. After the control zincated substrates had started plating in the Ni-P tank, a waiting mandrel loaded with previously sputter-seeded substrates was added to the array in a designated vacant position. The sputter-seeded substrates were immersed in the Ni-P tank with no intermediate treatment after storage for 10 weeks in air in standard polymer caddy containers used in the disk industry. Surface roughness was measured with a non-contact white light system.††† Plated Ni-P thickness was determined by X-ray fluorescence.

Results

Both RF and DC magnetron sputtered seed layers of Ni-P were effective in nucleating electroless nickel growth upon immersion in an electroless nickel plating bath. In each case, plated Ni-P retained the finish of the initial substrate. In other words, no new roughness was added. Significantly, as-plated Ni-P was essentially nodule-free, even for deposit thicknesses greater than 8 μm (315 μ-in.).

The catalytic activity of sputtered Ni-P remained effective for at least 10 weeks after sputtering. No special precautions were taken for storage of seeded substrates while awaiting electroless plating.

** *SEGI Model FA2-4TR 13.56 megahertz RF sputtering system, Semiconductor Engineering Group, Inc., Milpitas CA*

*** *OMG Fidelity Type 5023, OM Group, Inc., Cleveland, OH.*

**** *THôT Technologies Type 4224M, THôT Technologies Inc., Campbell, CA.*

† *FischerScope XUVM, Fischer Group, Fischer Technology, Inc., Windsor, CT.*

†† *Intevac Model 250B, Intevac, Inc., Santa Clara, CA.*

††† *ADE Phase Shift MicroXAM, ADE Phase Shift Div., ADE, Inc., Tucson, AZ.*

The comparison of surface roughness before and after Ni-P plating is shown in Table 1 for RF sputtering and in Table 2 for DC magnetron sputtering. Surface roughness, R_a, is expressed conventionally as the arithmetic average, R_a, of the peaks and valleys about an averaged centerline.

Seed-plate samples 1 thru 4 in Table 1 were first sputtered with a chromium binder layer followed by a sputtered Ni-P seed layer, and then Ni-P plated. For comparison, Table 1 also shows the R_a surface roughness of three initial aluminum substrates (samples 8 thru 10) from the same group as well as R_a for three substrates sputter-seeded but unplated (samples 5 thru 7).

Table 2 compares surface profile measurements of Type 5586 aluminum substrates simultaneously sputtered on each side in the DC magnetron system with R_a for similar substrates routinely processed by conventional double zincating. The only commonly shared treatment was the final step of Ni-P plating, described above.

Comparison of the initial substrate R_a (samples 8 thru 10, Table 1) with R_a after RF sputtering of binder and seed layers [samples 5 thru 7, 0.065 μm (2.6 μ-in) total] shows that the sputtered layers did not add roughness. Remarkably, R_a was also unchanged even after adding 8 μm (315 μ-in.) of Ni-P by electroless plating. Table 2 also shows R_a to be unchanged after plating Ni-P to a thickness of 9.4 μm (370 μ-in.) on a seed layer of Ni-P added by DC magnetron sputtering. In comparison, a three-fold increase in R_a surface roughness was noted for Ni-P simultaneously plated on the conventionally zincated control substrate.

The remarkable smoothness of seed-plate Ni-P may be seen in Fig. 1(a). The SEM photos in Figs. 1(a) and (b) are of areas of severe bending and maximum tensile stress produced in adhesion testing. In Fig. 1(a) (seed-plate), the plated Ni-P areas on either side of the bend test crack are smooth and essentially featureless, particularly in comparison with the control surface shown in Fig. 1(b).

The base of the crack in Fig. 1(a) is type 5586 aluminum alloy, as determined by energy dispersive X-ray element analysis. The bend test sample in Fig. 1(a) is from the group identified in Table 2 as "Cr / Ni-P sputtered / Ni-P plate." Fig. 1(b) shows a control bend test sample from the conventionally zincated group identified in Table 2 as "Zincated and Ni-P plated control."

Within the crack in Fig. 1(a), the bottoms of the jagged-edged Ni-P areas on each side remain strongly attached to the aluminum substrate. The close alignment of displaced opposing edge contours of adherent Ni-P within the crack suggests a complex fracture sequence. Ni-P in the control bend test [Fig. 1(b)] is also adherent but lacks material remaining attached on the crack bottom.

Discussion

Within the reproducibility of the methods used for measuring the parameters shown in Table 1, there was no significant difference between the average surface roughness of the as-received aluminum alloy 5586 substrate, R_a = 53.7 Å, and the roughness R_a = 55.5 Å after plating more than 8 μm (315 μ-in.) of Ni-P.

The smooth surface finish of seed-plated Ni-P at 1500X [Fig. 1(a)] was in striking contrast to the nodular Ni-P deposit on the conventionally zincated and simultaneously plated aluminum alloy control substrate [Fig. 1(b)], in agreement with a three-fold increase of surface roughness noted in Table 2. The wrinkled Ni-P surface area in Fig. 1(a) was produced by the adhesion bend test. Figs. 1(a) and (b) also show some surface contamination from handling.

Table 1
Average roughness R_a, Å; Initial substrate, 5586 aluminum; sputtered chromium thickness, 210 Å; sputtered Ni-P thickness, 440 Å; electroless Ni-P thickness in μm

Sample No.	Treatment	Electroless Ni-P thickness, μm	R_a, Å
1	Sputtered Cr/Ni-P+ electroless Ni-P plate	6.3	53
2	Sputtered Cr/Ni-P + electroless Ni-P plate	8.4	59
3	Sputtered Cr/Ni-P + electroless Ni-P plate	8.6	58
4	Sputtered Cr/Ni-P + electroless Ni-P plate	8.5	52
5	Sputtered Cr/Ni		49
6	Sputtered Cr/Ni		55
7	Sputtered Cr/Ni		55
8	Initial 5586 Al substrate		54
9	Initial 5586 Al substrate		55
10	Initial 5586 Al substrate		52

Table 2
Average roughness R_a, Å; Initial substrate, 5586 aluminum; sputtered chromium thickness, 300 Å; sputtered Ni-P thickness, 300 Å; electroless Ni-P thickness in μm

Treatment	Electroless Ni-P thickness, μm	R_a, Å
Initial Unplated 5586 Al substrate	----	22
Zincated and Ni-P plated control	13.0	65
Cr / Ni-P sputtered / Ni-P plated	9.4	22

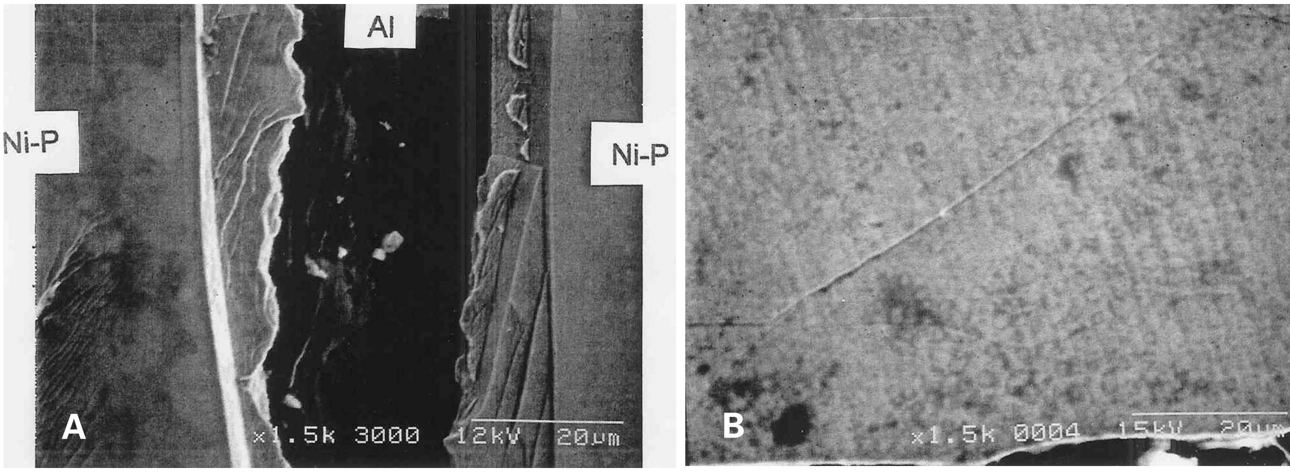

Figure 1—SEM photos of bend tests, 1500X: (a) seed plate (Cr / Ni-P sputtered / Ni-P plated), (b) control sample (Zincated and Ni-P plated control).

As indicated in Tables 1 and 2 and Fig. 1, the present seed-plate method permitted the growth of a thick Ni-P layer with no new roughness being added to that of the starting substrate. Also, the present seed-plate method is, in principle, not limited to aluminum and may have general usefulness for Ni-P plating on metals where zincating cannot be applied or is not effective.

Pre-polished metals may be of special interest for memory disk substrates since minimal final polishing of smooth seed-plate Ni-P would be required. From extensive experience with aluminum substrates, Ni-P is a texturable hard coating that also assists the formation of desirable properties of the magnetic layer.

According to Suenaga, *et al.*,[12] titanium is an ideal alternative memory disk substrate which can be highly polished to R_a = 1 Å. Since good adhesion of a deposit is generally promoted by surface oxide removal, it follows that some surface roughening may be expected if conventionally recommended acid etch treatments are applied to pre-polished titanium.[3] Suenaga, *et al.* avoided etching and instead prepared polished titanium and its alloys Ti-5Al-2.5Sn and Ti-6Al-4V for Ni-P plating by mechanical micro-roughening of the surface. Acceptable adhesion could only be obtained when polished titanium was roughened to a range of R_a between 2 and 60 Å and only if the Ni-P thickness was simultaneously limited to 5 μm (197 μ-in.) or less. Of interest, Suenaga, *et al.* also found that plated Ni-P did not adhere at all to very smooth titanium with initial roughness R_a less than 1.5 Å.

Looking forward, the seed-plate method offers a means to improve adhesion of electroless Ni-P on highly polished titanium, stainless steel and other non-magnetic alternative substrate materials.

For completeness, it should be mentioned that the initial capital cost of a sputtering system might be considered a disadvantage of the seed-plate method. However, while it is certainly true that sputtering equipment is expensive (typical of high vacuum, high voltage systems), the cost of sputtering per finished part is reasonable. An advantage of sputtering is that adhesion can be enhanced by brief operation in the reverse sputter-etch mode to remove surface oxide layers.

A disadvantage of sputtering equipment in general is that relatively close spacing is required between the flat source target and a preferably planar workpiece. Maximum spacing between the workpiece and the source target is typically 10 cm (3.9 in.) or less, dictated basically by the physics of ionization of argon gas plasma at low pressure. Details of the sputtering process may be found in texts on vacuum technology and plasma physics.[13]

For Ni-P on aluminum alloy disk substrates, cost savings of about 25 to 30% are conservatively estimated for replacing conventional double zincating by the seed-plate method. Cost calculations include the capital expense of new sputtering equipment. Recalling that the basic purpose of polishing is to remove nodular Ni-P, cost savings are available from reduced polishing of already smooth, nodule-free, as-plated Ni-P. Savings may also be contributed if less material removal by polishing allows for thinner Ni-P deposits and extended Ni-P bath life. If substrate blanks are first mechanically pre-smoothed before sputtering so as to take advantage of conformal Ni-P deposition provided by the seed-plate method, an overall analysis should also take into account manufacturing costs to achieve the initial smooth finish.

Without zincating and associated types of defects, expected yield increases should contribute to additional cost savings, if included in a more refined cost model. Cost analysis should include savings from reduced materials and energy requirements and also reduced use of deionized rinse water on the plating line and at polishing stations. Waste water treatment volumes will also be significantly reduced. Looking forward with some speculation, substantial cost benefits are anticipated where the single preparation step of the seed-plate method can replace multi-step, expensive activation for Ni-P plating on glass, ceramics and polymers.[14]

Conclusions

The very smooth Ni-P deposits obtained with the seed-plate method are remarkable in themselves but also raise the question as to whether nodular growth is to be expected as an inherent aspect of Ni-P deposition. From a very general viewpoint, the present seed-plate results suggest that nodular growth somehow requires interaction between non-uniformities in the metal surface and the chemistry of etch solutions at the various stages of conventional surface preparation. For aluminum, the few hundred Angstroms of sputtered binder and seed layers are apparently sufficient to cover and hide intermetallic inclusions and cold-worked regions, thereby preventing nodule formation from being initiated by these non-uniformities.

It should be mentioned that other means for minimizing nodular growth have also been disclosed, based on additions of metallic ions to the chemistry of zincating and also to the Ni-P plating bath.[15,16] It may be fairly stated that fundamental studies are needed for improved understanding of all mechanisms leading to smooth Ni-P deposition and minimal nodule growth.

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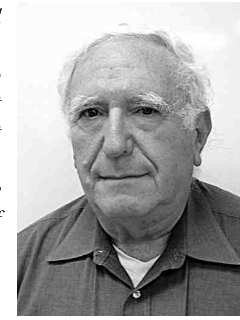

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Answers to I.Q. Quiz #412

1. Nickel sulfate provides the bulk of the nickel ion content.

2. The sulfate is used because it is stable, *i.e.*, neither reduced at the cathode nor oxidized at the anode. And, it is cheap.

3. Though it provides a minority of nickel ion, the chloride serves to prevent the nickel anode surface from passivating, promoting proper anode corrosion.

4. The properties of the nickel deposits would be sensitive to the presence of the "non-nickel" cations such as sodium or potassium.

5. Boric acid serves as a weak buffer to maintain the pH of the cathode film and stabilize the plating environment.