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The effects of stabilizers on the bath stability of electroless Ni deposition and the deposit

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It is demonstrated that the addition of thiourea and maleic acid significantly improved the stability of the EN bath. It was observed that the stabilizers have a minor and a major effect on phosphorus content and morphology of the EN deposits, respectively. It is also shown, for the first time, that the addition of the stabilizers has an effect on the nano-grain size of the EN deposit.

PACS codes: 81.15

Keywords: Electroless nickel; stabilizers; characterization; nano-grains

Introduction

Electroless nickel (EN) deposition has become commercially important for finishing steel, aluminum, copper, plastics and many other materials[1]. In this process, metal deposition is driven by the catalytic oxidation of the reductant on the substrate surface[2]. Major advantages over the electrodeposition process include the formation of a uniform deposit on irregular surfaces, direct deposition on surface activated non-conductors, and the formation of less porous, more corrosion resistant deposits. However, sudden bath decomposition can result in an increase in costs and the production of environmentally hazardous pollutants due to the large waste generation.

To overcome the problems related to the bath decomposition, EN deposition solutions normally contain trace amounts of stabilizers to prevent the homogeneous reactions that trigger the random decomposition of the entire bath[2].

The overall reaction of the nickel reduction by hypophosphite can be expressed as follows[3]:

In the reaction (1), nickel ions in the EN solution are reduced by the electrons generated through the oxidation of hypophosphite ions. The beginning of the electroless nickel deposition is known to be controlled by the anodic processes, and the first step involves a non-Faradaic step, namely the adsorption of hypophosphite on the catalytic surfaces (reaction (2))[4]. Some stabilizers function through the preferential adsorption (poisoning) to the catalytic surface. Thus, stabilizer present even in trace quantities may dramatically slow down the rate of the hypophosphite oxidation[5]. The oxidation of hypophosphite ion on a catalytic substrate can be described as follows[4]:

67

68 In the reaction, the adsorption of hypophosphite on the catalytic surfaces (reaction (2)) is
69 followed by the homolytic breakdown of P-H bond (reaction (3)). An intermediate radical,
70 $\text{HPO}_2^{\cdot -}$, is easily oxidized to yield orthophosphorus and hydrogen gas in the presence of
71 the catalytic metal of the platinum group[4]. The hydrogen overvoltage on a metal
72 surface may be taken as a measure of the ease of hydrogen discharge on a metal surface,
73 and the addition of stabilizer(s) increases the hydrogen overvoltage of the surface thereby
74 making the hydrogen discharge difficult[6,7].

75

76 A number of different types of effective stabilizer for electroless nickel deposition have
77 been identified[2,8,9]. These include:

- 78 1. Compounds of group IV elements (i.e. Se, Te, thiourea, MBT, thiocyanate, etc);
- 79 2. Unsaturated organic acids (i.e. Maleic, itaconic, etc);
- 80 3. Heavy metal cations (i.e. Sn^{2+} , Pb^{2+} , Cu^{2+} , etc);
- 81 4. Oxygen containing anions (i.e. AsO_4^{3-} , MoO_4^{2-} , etc);
- 82 5. Some classes of surfactants, dispersants of various charges, and emulsifying
83 agents (i.e. Potassium perfluoroalkyl sulfonates, lauryl trimethyl ammonium
84 chloride, N-Oleoyl betaine, etc.)[9].

85

86 The ability of these compounds to stabilize the electroless plating bath is influenced by
87 several parameters such as their concentration, pH, temperature, solution fluid dynamics,
88 the concentration of reducing agents, and the presence of foreign bodies[10]. Of these,
89 the stabilizer concentration is considered to be the most crucial parameter[11]. Each

90 stabilizer characterizes of an optimum concentration depending on the characteristics of
91 the metallic coating desired. In addition, stabilizers can have more than one influence on
92 the bath performance and, depending on their concentration, can act as accelerators[7,12-
93 14] or inhibitors of the deposition[1-3,10,13,15-19]. In addition, they can lead to the co-
94 deposition of S and Pb[13,15,20], act as brighteners and/or leveling agents[12], and may
95 also influence the P content in the deposit[15].

96
97 The characteristics of electroless Ni-P binary alloy deposits are dependent upon the
98 chemical balances in the metallization solution, especially the pH of the bath, and the
99 type of stabilizer [21]. Deposit characteristics such as morphology, phosphorus content
100 and the distribution of phosphorus can influence the subsequent degradation behavior in
101 aggressive environments such as those containing chloride[21].

102
103 The use of heavy metal stabilizers at relatively low pH values (4.0 & 4.5) favors the
104 formation of deposits having a smooth topology and layered morphology[22]. The
105 phosphorus content of the deposits tends to be high (> 10 %), and at high corrosion
106 potentials, pitting corrosion can occur. This very localized high aspect ratio attack (~100)
107 can damage and penetrate the substrate[21]. By contrast, the use of a thio-derived
108 stabilizer at a relatively high pH value (~5) for an acid EN bath produces a deposit having
109 'cauliflower-like' appearance and fibrous morphology[22]. The phosphorus content is
110 relatively low (< 6 %) and uneven corrosion takes place at the micron level, giving the
111 surface a blackish appearance. However, it is far less penetrating than the former[21].

This paper presents our investigation of bath stability using two distinctive stabilizers. In addition, we have studied the changes in morphology, nano-crystal size, composition, and phase of the Ni-P binary alloy deposits produced from the stabilized electroless nickel metallization system.

Experimental

2.1. Materials & Reagents.

Cu foil (99.98%, Aldrich Chemical Co.), 20 mm X 10 mm X 0.1 mm, was used as the substrate. Prior to immersion in the plating bath, the copper substrate was etched with 5 % H_2SO_4 at room temperature for 60 sec[19].

Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 98.2 %), Sodium Acetate (CH_3COONa , anhydrous, 99.0 %), Sodium Carbonate, and thiourea were purchased from Caledon. Sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) and maleic acid were obtained from Sigma-Aldrich Chemical Co. Nitric acid was purchased from Anachemia while sulfuric acid (reagent A.C.S.) and hydrochloric acid (reagent A.C.S) were purchased from Fisher-Scientific.

Deionized water with a resistivity of greater than $15 \text{ M}\Omega \text{ cm}$, generated using a Millipore Elix10 purification system, was used for solution preparation and the rinsing of glassware. The beakers used for the deposition reaction were cleaned separately since they required an overnight acid wash in 40 % nitric acid to eliminate any surface-adsorbed metal nuclei.

Electroless deposition of Ni-P on the copper foil substrates was achieved by immersing the substrates in an acidic hypophosphite bath with the following compositions: Nickel sulfate (30 g/L); Sodium hypophosphite (20 g/L); Sodium acetate (20 g/L); the initial pH was adjusted by addition of hydrochloric acid (5 %). The stabilizers were added at a number of different concentrations; thiourea ranged from 0.1 to 5.0 mg/L and maleic acid varied from 0 to 3000 mg/L.

2.2 Apparatus and Experimental Procedures.

2.2.1 Measurement of *Deposition Rate*. 100 mL Pyrex glass beakers were used for the deposition rate and stability experiments. 80.0 mL of the plating solution was added to the beaker immersed in a NESLAB GP-200 temperature regulated water bath. The temperatures of the water bath and the plating solution were controlled within 1 °C throughout the experiments. The plating conditions employed were pH 4.5, temperature 85 (+/- 1) °C, a plating time 2.0 h, and a bath load 0.491 dm²/L. The nickel-plating solution was not agitated during the deposition process.

When the temperature reached the preset value, the pretreated copper foil substrate was in the solution. Electroless nickel plating was induced catalytically on copper surface by touching the substrate with a copper wire on which a Ni-P deposit had been previously deposited. After 2.0 h, the specimen was removed from the bath, rinsed with deionized

water, air-dried, and weighed on an analytical balance (OHAUS AP250D) with a precision of $\pm 10 \mu\text{g}$.

The deposition rate, R , can be expressed as a weight gain and calculated using the equation,

$$R = (\omega \cdot 10^4) / (\sigma A t) \quad (\text{Eq.1})$$

where R is the deposition rate [$\mu\text{m/h}$], ω is the weight gain [g], σ is the density of the deposit analyzed from energy dispersive spectroscopy (EDS) [g/cm^3], A is the surface area of the substrate [cm^2], and t is the deposition time [h]. The experimental results reported in this work are the average values of triplicate measurements.

2.2.2 Bath Stability Test. The Pd stability test method [19,23-26] was used to determine the effect of stabilizer concentration on the stability of the bath. This test was conducted at the lower temperature of $65 \pm 1^\circ\text{C}$ to amplify the difference in the stabilities of the plating solutions. When the solution reached $65 \pm 1^\circ\text{C}$ and became functional (hydrogen gas evolution was observed from the etched electroless Ni-P deposited Cu foil), 1.00 mL of 40.0 mg/L PdCl_2 was added drop by drop over 25 sec to the 80 mL EN plating solution. The time required for the solution to be decomposed was recorded. The end point, or the onset of bath decomposition, was defined as the time when the solution became dark

green and opaque. The experiments were performed at least 3 times in order to confirm the reproducibility of the results.

2.2.3 Surface Analysis.

The surface morphology of the Ni-P deposits was investigated using scanning electron microscopy (Hitachi S3500N electron microscope). Energy Dispersive X-ray spectrometry (IncaEnergy 400, Oxford Instrument Ltd.) was used to analyze the Ni and P content (wt %) of the Ni-P deposits. The entire 1.2 X 1.2 mm² area was scanned to enhance the reliability instead of randomly selecting only several small spots for the analysis. The crystallinity of the deposit was investigated by X-ray diffractometry (Philips X'Pert). The X-ray diffraction using Cu-K α was operated at an accelerating voltage and current of 45 kV and 40 mA, respectively. Transmission electron microscopy (Philips CM12 CTEM) and selected area electron diffraction (SAED) were used for the microstructural analysis of the Ni-P deposits.

Results and Discussions

3.1 Deposition Rates. The deposition rates were measured in the presence of various concentrations of the two stabilizers (section 2.2.1). This rate was calculated from the deposit density, obtained from EDX analysis, and the weight gain. For thiourea the concentration range studied was 0.0-5.0 mg/L, and the deposition rates were in the range of 9.0 $\mu\text{m/h}$ to 15.4 $\mu\text{m/h}$ (Figure 1). The deposition rate increased with increasing

203 stabilizer concentration, and reached a maximum at 2.2 mg/L. The critical concentration,
204 when the electroless Ni-P deposition ceased, was between 3.0 and 5.0 mg/L thiourea.
205 Beyond the critical concentration, the catalytically induced initiation of the electroless
206 Ni-P deposition process could not be achieved.

207
208 A gradual increase in the rate of nickel deposition followed by a decrease is consistent
209 with the result observed by others[27]. The enhancement of the nickel deposition at low
210 stabilizer concentration might be caused by the thiourea participation in the formation of
211 the reactive intermediate that facilitates the oxidation of hypophosphite ion thus
212 accelerating the overall electroless nickel deposition[28]. The decrease in the deposition
213 rate at high concentration was attributed to a reduction in the number of catalytic sites on
214 the metal surface due to formation of a thin film of adsorbed thiourea on top of the
215 catalytic surface[19]. While both the opposing factors contribute to the deposition rate
216 throughout the entire concentration range, the experimental results suggest that the
217 oxidation of hypophosphite ion is dominant at a lower thiourea concentration while the
218 reduction in the catalytic sites become dominant when the concentration exceeds 2.2
219 mg/L. This is understandable as there exists an abundance of catalytic sites, namely,
220 unoccupied surface, at relatively low concentrations of thiourea.

221
222 On the contrary, the effect of maleic acid on the deposition rate was insignificant: Only a
223 slight change of about 2.45 $\mu\text{m/h}$ in the deposition rates was observed over a very wide
224 concentration range, 0-3000 mg/L (Figure 1). This result suggests that one advantage of

using maleic acid as a stabilizer is that a consistent deposition rate can be achieved without the need to precisely control and adjust the stabilizer concentration.

3.2 Bath Stability. The Pd stability test showed a significant increase in bath stability with the addition of either thiourea or maleic acid. For thiourea the bath life increased from 1.3 ± 0.5 min to >264 min as the stabilizer concentration was increased from 0.5 mg/L to 2.0 mg/L (Figure 2a). For stabilizer concentration < 0.5 mg/L, the bath stability was not observably affected. The bath containing a thiourea concentration higher than 2.6 mg/L could not be tested since, at the lower operating temperature employed in the stability test, 65 °C, the Ni-P deposition could not be initiated. An abrupt increase in the Pd stability of the bath was noticed between 1.5 mg/L and 2.0 mg/L thiourea.

For the maleic acid stabilizer, the increase in the Pd stability in the lower concentration region, 0 mg/L to 300 mg/L was steeper than that in the higher concentration region, 300 mg/L to 3000 mg/L (Figure 2b). The Pd stability test results of maleic acid indicated that the bath life has increased from 0.7 ± 0.1 min to 101 ± 9 min over the range studied.

3.3 Surface Morphology and Phase Composition. It is claimed that the corrosion performance of an electroless Ni-P deposit, to a large extent, is determined by its structure[29] while the surface topography is strongly dependent on the characteristics of electroless nickel-plating solution[26]. The effects of the various concentrations of the two stabilizers on the morphology of the deposits are shown in Figures 3 & 4. The horizontal ridges in the SEM micrographs outline the underlying copper substrate

morphology. The surface produced with no stabilizer was very smooth (Figure 3a), but started to become nodular with 0.3 mg/L thiourea (Figure 3b). The nodular structure (“orange peel” shape) became more evident with a 1.3 mg/L addition of thiourea (Figure 3d), and small pits developed on the surface. This nodular structure completely evolved into a cauliflower-like structure when the thiourea concentration was increased to 2.0 mg/L (Figure 3f). The transition between nodular and ‘cauliflower’-like structure is apparent at 1.5 mg/L (Figure 3e).

Ripple like structures were formed on the surface of a Ni-P deposit with the addition of 40 mg/L and 80 mg/L of maleic acid (Figure 4a&b). A surface smoothing effect was observed at 180 mg/L and 300 mg/L maleic acid (Figure 4c&d), the surface becoming as smooth as the one with no stabilizer (Figure 4a). Small nodules started to form at a stabilizer concentration of 2000 mg/L (Figure 4e), and became more evident at 3000 mg/L maleic acid (Figure 4f).

Low Angle XRD analysis indicated one broad peak at $\sim 44.5^\circ$ for the whole series of deposits. The peak position is that expected for the Ni (1 1 1) plane. The full width at half maximum (FWHM) was obtained from Gaussian fitting. The maximum difference in the full width at half maximum (FWHM) was $\sim 1.4^\circ$ (Figure 5 & 6). The broadening of a peak in XRD indicates that the deposit can either be amorphous or refined crystalline.

The transmission electron microscopy (TEM) was used to clarify the deposit structure. The TEM micrographs and the electron diffraction patterns of as-plated Ni-P alloy

deposits at various concentrations and types of stabilizers (Figure 7) indicated that the EN deposits were composed of nanocrystals with different orientations. The smooth morphology of the EN surface (from SEM) produced without stabilizer was actually composed of fine crystals of relatively uniform diameter (2-5 nm) evenly distributed throughout the entire surface (Figure 8a). The diffraction pattern showed two diffused inner rings and three weak outer rings, indicating a polycrystalline face centered cubic (FCC) structure (Figure 7a). The diffraction rings are assigned in the diffraction pattern (Figure 7). The inner ring became diffuse with the addition of thiourea stabilizer (0.9 & 1.3 mg/L), which indicated the presence of larger number of smaller nanocrystals (Figure 7b). The grain size distribution was obtained using an image analysis program (Image-Pro Plus).

The changes in the grain size distribution with the addition of the stabilizer are shown in Figure 8. It is shown that the addition of 0.9 mg/L thiourea produces more smaller grains (Figure 8b) compared to the deposit produced from the solution with no stabilizer. Both spot and weak ring diffraction patterns were observed for the deposit from the EN solution with 2.0 mg/L thiourea (Figure 7c&d). This implies the presence of much larger crystals in the deposit. The grain size distribution graph (Figure 8c) indicated that a small number of crystals larger than ~20 nm and ~30 nm in diameter were present in the deposit, which were not observed in any other deposits. Moreover, an increased number of grains larger than 5 nm was observed. The size distribution results in Figure 8 are consistent with the XRD results. The differences in the FWHM were ~1.4° (Figure 6), and the deposits produced from the solution containing intermediate concentrations of

thiourea possessed larger FWHM at 2θ angle of $\sim 44.5^\circ$ than those obtained from solutions with no additives and at a 2.0 mg/L concentration. These changes might be caused by the peak broadening due to changes in the size distribution of grains (Figure 8).

XRD analyses of the deposits produced from the solution containing maleic acid also indicated one peak at a 2θ angle of $\sim 44.5^\circ$ with the differences in FWHM of $\sim 1.28^\circ$ (Figure 6). TEM BF images (Figure 7 a, e, f, & g) showed a decrease in the grain size as the concentration of maleic acid increased. The grain size distribution is shown in Figure 8a, d, e, & f. A reduction in the number of larger grains is observed, while the % grains of $\sim 1\text{-}2$ nm size increased significantly from 40 % to 72 %.

The selected area electron diffraction pattern showed diffuse rings and weak outer rings, indicating polycrystalline structures which were similar to the ones with thiourea, but the diffused rings were slightly broader. This is attributed to the larger number of smaller sized crystals with maleic acid, as shown in Figure 8. The diffuse ring and the weak outer rings contained intense diffraction spots in the diffraction ring for the deposit with 3000 mg/L maleic acid. This inhomogeneous ring pattern represented highly oriented crystals. Fine crystals are very difficult to observe from the TEM BF image, indicating either the presence of finer crystals than those from thiourea stabilizer or less likely to be crystals grown parallel to the deposit surface.

In the selected area diffraction pattern analyzed, one very weak ring with a d value of $\sim 1.53 \pm 0.08$ is not assigned since it is the only peak that doesn't match the FCC crystal

ring pattern and exists in only some SAD patterns of even the same sample. The conditions existing during electroless nickel deposition do not permit the formation of intermetallic compounds. Thus, the elemental phosphorus is trapped between nickel atoms non-uniformly[2]. The elemental phosphorus can have d-values of 1.63, 1.61, and 1.40, and the atomic P content is ~10 %. Thus, the weak ring pattern may be attributable to the elemental P trapped in the Ni matrix

3.4 Elemental Composition of the deposit. Electroless nickel deposition by hypophosphite is generally expressed according to reaction (1). During the electroless nickel deposition process, phosphorous is co-deposited with nickel by secondary reactions[2]. There appears to be three possibilities. In the atomic hydrogen mechanism, the hypophosphite anion is reduced by adsorbed atomic hydrogen on the catalytic surface to yield phosphorus, water, and hydroxyl ion[5]:

In the electrochemical mechanism, elemental phosphorus is produced by direct cathodic reaction of hypophosphite,

Thirdly, in the Cavollotti and Salvago's mechanism, the direct interaction of the catalytic nickel surface with hypophosphite gives rise to the codeposition of phosphorus[30]:

340

342

343 where $\text{NiOH}_{\text{ad}}^+$ represents a hydrolyzed Ni^+ species adsorbed at the catalytic surface.

344

345 An increase in the phosphorus content in Ni-P coatings (from 6.6 to 13.4 % wt) was
346 shown to be accompanied by an amorphization of their structure[31], suggesting that an
347 electroless Ni-P deposit can be either polycrystalline or amorphous depending on the P
348 content. The phosphorus content (wt %) is one of the important factors determining the
349 structure of deposits. It was reported that an electroless Ni-P deposit containing 3-7.3 % P
350 could form a crystalline structure, and a Ni-P deposit containing less than 8.5 % (wt %) P
351 would form a microcrystalline structure. In addition, Ni-P deposits containing more than
352 8.5 (wt %) P were found to be amorphous in structure[3]. The effects of the stabilizers on
353 the P content of the coating have been studied using Energy Dispersive X-ray (EDX)
354 analysis to determine the P content. The results are plotted in Figure 9. The Phosphorus
355 contents ranged from 5.90 % to 8.42 % and 7.47 % to 8.94 % for the deposits produced
356 from the baths containing thiourea and maleic acid, respectively. The deposits produced
357 from the plating baths containing more than 2.0 mg/L thiourea indicated a low P (wt %)
358 content, < 7 %. As discussed in the section 3.3, the deposit consisted of crystals of larger
359 size. Considering the uncertainty of ~0.5 % due to the EDX instrumental limitation, the
360 coating composition remained relatively constant for maleic acid with in a wide
361 concentration range, 0 mg/L to 3000 mg/L.

362

3.5. Causes of the changes; functions of the stabilizers

The initial stage of electroless nickel growth was found to follow an island type growth. The growth begins at certain active sites, and continues isotropically resulting in hemispherical islands of nickel phosphorus. These islands continue to grow larger until they join and coalesce each other[32]. During the electrochemical deposition process, new grains will grow if the size of an initial cluster exceeds the critical dimension N_c . The larger the N_c , the more favorable it is for the growth of a single crystal from a previously nucleated seed grain. The critical dimension N_c for a 2D-like nucleus can be described as follows[33]:

$$N_c = \frac{bs\varepsilon}{(Ze\eta)^2}, \quad (\text{Eq. 2})$$

where s , ε , Z , η , and b are the area occupied by one atom on the surface of the nucleus, the edge energy, the effective electron number, the overpotential and a constant, respectively.

The addition of stabilizers such as thiourea[20] and maleic acid[15] tends to increase the open circuit potential during the deposition and deposition potential obtained from an anodic and a cathodic half cell reactions, respectively, since the stabilizers adsorb to the catalytic free nickel surface and thereby decrease the rate of the charge transfer reaction. The increase in deposition potential can be caused from three possible influences: A. acceleration of cathodic kinetics, B. suppression of anodic kinetics, and C. changes in

both cathodic and anodic kinetics. According to Das & Chin (1996)[15], maleic acid influenced both cathodic and anodic half reactions. From the above equation, the increase in the overpotential decreases N_c . This will enhance the nucleation process, resulting in an increasing number of smaller sized grains. This is well illustrated with maleic acid stabilizer. As the concentration increases, the number of small sized grains is increased (Figure 7 & 8). The only exception was deposit produced from the solution containing 2.0 mg/L thiourea where the number of large particles actually increased. This may be attributed to the strong adsorption of sulfur anions on the crystal surface. Macheras et al.[34] have claimed that the hydrogenolysis of the C-S and S=O bonds produces sulfur anions, which inhibit the crystal growth in a particular direction; Macheras et al. attribute the predominance of the [1 0 0] texture in their electro-nickel deposit to the specific adsorption of the sulfur anions on the (110) crystallographic direction leading to a suppression of growth in this plane[34]. It seems that when the thiourea concentration increased from zero to 2.0 mg/L, a large number of sulfur anion is produced. These sulfur anions will make an orientation-specific adsorption which favors the crystal growth of a particular orientation. As a result, an increased formation of larger crystals is observed (Figure 8c).

Azumi et al.[35] also observed similar phenomena on a larger scale. It was indicated that laterally limited Ni-P layer growth would lead to deposition in a columnar form on a flat surface of a substrate. In his experiment, broken as well as spherical Ni-P particles in the plating solution were filtered, analyzed and showed both radial growth and laterally limited columnar growth[35]. Salvago et al. (1980) reported that the thio-derived

stabilizer, MBTA, caused growth with a mainly columnar 'cauliflower' like morphology[22] instead of stratified layer type morphology. A similar columnar 'cauliflower' like morphology was obtained in our case from the deposition solution containing thiourea greater than 2.0 mg/L. In other words, at these concentrations of the thiourea stabilizer, the Ni-P layer growth is laterally limited due to the presence of the stabilizer, resulting in a columnar form of Ni-P deposit. In addition, the increased number of larger sized crystals with 2.0 mg/L thiourea is attributed to the sulfur adsorption induced laterally inhibited growth of the particles.

Conclusion

The addition of thiourea and maleic acid significantly improved the Pd stability of the EN bath. In addition, an enhancement of the deposition rate was observed for thiourea, and it reached a maximum of 15.4 $\mu\text{m/h}$ at 2.2 mg/L thiourea. Unlike thiourea, deposition rates in the presence of maleic acid stabilizer indicated no significant change.

Significant surface morphological changes were observed in the "as plated" electroless nickel deposits in the concentration ranges studied for thiourea and maleic acid. At high thiourea concentration, the P (wt %) content decreased to less than 7 %. Moreover, nodular surface was converted to 'cauliflower' like surface. A Surface smoothing effect was observed with the addition of 180 mg/L and 300 mg/L maleic acid, and nodular surface appeared at high maleic acid concentration.

Low Angle XRD analysis indicated one broad peak at $\sim 45^\circ$ for the series of deposits. The full width at half maximum was between 6.25° and 7.25° . TEM image and SAD patterns of Ni-P alloy deposits at various concentrations and types of stabilizers showed both 'amorphous like' and FCC polycrystalline microstructure due to the formation of nanocrystals.

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Figure captions

Figure 1. Effect of thiourea and maleic acid concentrations on the deposition rate of the electroless nickel system

Figure 2. Effect of (a) thiourea and (b) maleic acid concentration on Pd stability of the electroless nickel system

Figure 3. SEM micrographs of the electroless Ni-P deposits from the plating solution with different concentration of thiourea stabilizer. All of these micrographs have the same magnification of 2000x. The black lines in the SEM micrographs indicate 20 μm .

All other parameters are also indicated in the SEM micrographs.

Figure 4. SEM micrographs of the electroless Ni-P deposits from the plating solution with different concentration of maleic acid. All of these micrographs have the same magnification of 2000x. The black lines in the SEM micrographs indicate 20 μm . All other parameters are also indicated in the SEM micrographs.

Figure 5. Low angle XRD patterns of Ni-P binary alloys deposited from EN bath with and without stabilizers

Figure 6. Full Width at Half Maximum (FWHM) of the peak of 2θ of $\sim 45^\circ$ for various concentrations of thiourea and maleic acid

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534 Figure 7. Transmission electron micrographs (TEM) and the selected area diffractions
535 (SAD) patterns of Ni-P binary alloy deposits at various concentration and types: (a) no
536 stabilizer, (b) 0.9 mg/L thiourea, (c) & (d) 2.0 mg/L thiourea, (e) 40 mg/L maleic acid, (f)
537 180 mg/L maleic acid and (g) 3k mg/L maleic acid

538

539 Figure 8. Effect of stabilizers of various concentrations on grain size of the Ni-P binary
540 deposits

541

542 Figure 9. Effect of thiourea and maleic acid on phosphorus content in the electroless
543 nickel deposit

Figure 1

Figure 2(a)

Figure 2(b)

Figure 3(a)

Figure 3(b)

Figure 3(c)

Figure 3(d)

Figure 3(e)

Figure 3(f)

Figure 4(a)

Figure 4(b)

Figure 4(c)

Figure 4(d)

Figure 4(e)

Figure 4(f)

Figure 5

Figure 6

Figure 7(a)

Figure 7(b)

Figure 7(c)

SAD

Figure 7(d)

Figure 7(e)

Figure 7(f)

Figure 7(g)

Figure 8(a)

Figure 8(b)

Figure 8(c)

Figure 8(d)

Figure 8(e)

Figure 8(f)

Figure 9