Journal of The Electrochemical Society, **150** (11) C816-C822 (2003)
0013-4651/2003/150(11)/C816/7/$7.00 © The Electrochemical Society, Inc.

Mechanism of Stabilizer Acceleration in Electroless Nickel at Wirebond Substrates

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This paper examines the mechanism of stabilizer concentration at electroless nickel wirebond electrodes. A one-step activation protocol was first achieved on copper substrates using acetic acid and dimethylamineborane. Thereafter nickel multilayers were grown onto the substrates using nickel sulfate heptahydrate as the source of nickel, sodium hypophosphite as the reducing agent, acetic acid as the complexing agent, and thiourea/lead acetate as the stabilizing agent. The morphology of the nickel layers and the effective concentration of the stabilizer were determined using quartz crystal microbalance, gravimetric techniques, and energy-dispersive X-ray analysis (EDX). The plating rate was obtained by measuring the thickness of the Ni-plated using X-ray fluorescence spectroscopy. It was found that lead acetate completely inhibited the plating, and a bimodal distribution was observed as the concentration of the thiourea was varied. We proposed a mechanism for the effect of stabilizer in electroless Ni baths. This mechanism was confirmed using Fourier Transform Infrared and EDX measurements.

Manuscript submitted March 24, 2003; revised manuscript received June 2, 2003. Available electronically October 2, 2003.

Electroless plating is widely used in a variety of applications such as electronics packaging, jewelry making, and as a suitable finish for mounting chips to chip carriers. Nickel electroless deposits have been reported to exhibit high corrosion resistance in various media.[1] Commercial electroless nickel solutions contain several components including nickel salts, chelating agents, buffers, accelerating agents, stabilizers, and pH adjusters. Each component serves a specific purpose and the balance of each species must be maintained throughout the bath lifetime. During the deposition process, two main reactants must be continually replenished. These are the nickel ions and the reducing agent. Much effort is going into studying means of prolonging the lifetime of electroless nickel baths, removing any by-products and replacing toxic components.[1]

The protective coatings of Ni deposits significantly depend on the stabilizers added to the electroless nickel plating baths, pH, and the substrate type.[2,3] Spontaneous decomposition of electroless plating baths can be virtually eliminated or controlled by the addition of a small amount of stabilizers or inhibitors. Stabilizers are chemical agents in electroless plating baths required to prevent the homogeneous reaction that triggers the spontaneous decomposition of an entire plating operation.[1,2] The catalytic nature of the substrate to be coated can be significantly modified using trace concentrations of these stabilizers. At low stabilizer concentrations, substrate activity can be significantly enhanced to produce an increase in deposition rate. At low thiourea concentration, metal dissolution occurs. Beyond a critical level, the stabilizer may poison the substrate, thus completely inhibiting the catalytic activity. Consequently, it is important to determine the effective concentration of the stabilizer for specific bath chemistry.

The determination of the effective stabilizer concentration has been achieved mainly by trial and error. Some of the methods that have been reported for determining this parameter include polarization techniques and the measurement of deposition rate *vs.* stabilizer concentration.[4-6] Another is the measurement of the time prior to visible formation of black precipitate by adding potassium chloride solution.[7] Using any of these methods, the effective or critical stabilizer concentration was reported to vary from 0.1 ppm to several milligrams/liter.[4-7] A very sharp maximum is usually recorded by measuring the deposition rate *vs.* stabilizer concentration. The critical stabilizer concentration (CSC) is indicated by the cessation of the plating reaction and this is evidenced by the loss of hydrogen evolution.

Previously, we have studied the interaction of the reactive, boron-containing intermediates, which were generated *in situ* from dimethylamineborane DMAB solutions at gold surfaces. Using mass sensors, we have correlated the bath chemistry with the overall plating quality on industrial wirebond samples.[8-10] We also tested the ability of the sensors to monitor the bath chemistry during plating using ten different bath formulations, and have these correlated plating rates with thickness on industrial laminate chip carrier (LCC) wirebond samples.[9] In this work, we have investigated the effective concentration of the stabilizer as well as examined the mechanism of the stabilizer regeneration in the electroless plating deposition of Ni on Cu/Ni substrate. The CSC was studied at relatively low (~0.01 ppm) concentration of thiourea and a regeneration mechanism is proposed.

Experimental

Reagents.—All reagents were of analytical grade and were used as received except otherwise stated. $NiSO_4 \cdot 7H_2O$, $NaH_2PO_2 \cdot H_2O$, lead acetate trihydrate, thiourea and DMAB were obtained from Acros, Inc. (Pittsburgh, PA), and acetic acid (HAc) from Sigma Chemicals (St. Louis, MO). All solutions were prepared using deionized (DI) water with resistivity of 17 MΩ or higher. The QCM measurement was performed at 80°C. The temperature was kept constant with a Haake (Lachat Instruments, Milwaukee, WI) water bath. The quartz crystal worked well at this temperature.

Instrumentation.—All microgravimetric quartz crystal microbalance (QCM) experiments were performed using QCA 917 quartz crystal analyzer (Seiko EG&G). An open-circuit system was used for QCM measurements in which only the gold-coated, quartz crystal working electrode was connected, but in the absence of auxiliary and reference electrodes. The Au-coated quartz crystals (AT-cut, 9 MHz) having 0.2 cm^2 geometric area per face were obtained from EG&G Instruments (Princeton Applied Research). The resonant frequency was determined using QCA 917 quartz crystal analyzer (Seiko EG&G). The electrodes consisted of 1000 Å of gold film on a polished quartz with a texture of $\leqslant 1$ μm and a 50 Å chromium adhesion layer between the electrode and the quartz. The surface morphology and qualitative analysis of the nickel deposits were determined using scanning electron microscope (SEM, Phillips-Electroscan, model 2020), which is equipped with a Link ISIS energy dispersive X-ray analysis (EDX) analyzer.

Bath composition.—The starting composition and concentrations of the electroless Ni plating baths that we studied included: 6 g/L Ni^{2+}, 30 g/L $NaH_2PO_2 \cdot H_2O$, 30 g/L HAc, and 0.05 ppm thiourea. When the effect of one component was investigated, its concentration was varied while other parameters were kept constant. NH_4OH

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Table I. Composition and operating conditions for nickel hypophosphite bath at variable stabilizer concentrations.[a]

Bath constituents	g/L
$NiSO_4 \cdot 7H_2O$	6.0
$NaH_2PO_2 \cdot H_2O$	30.0
Thiourea	Variable (0-2 ppm)
Acetic acid	30.0
pH	5.1
Temperature	82°C

[a] No plating was recorded when lead acetate was used as bath stabilizer.

Table II. Composition and operating conditions for nickel hypophosphite bath at variable nickel ion concentrations.[a]

Bath constituents	g/L
$NiSO_4 \cdot 7H_2O$	Variable (1-12)
$NaH_2PO_2 \cdot H_2O$	30.0
Thiourea	0.05ppm
Acetic acid	30.0
pH	5.1
Temperature	82°C

[a] No plating was recorded when lead acetate was used as bath stabilizer.

was used to adjust pH to 5.1. The bath temperature was kept at 82°C and the plating time lasted 30 min. Tables I, II, and III provide a summary of the compositions of all baths studied.

Electroless deposition.—In this study, we used utilized LCC wirebond substrates from IBM Microelectronics, Endicott, NY. The LCCs were circuitized with copper, and were used as the substrates for the electroless Ni plating. Because Cu could not catalyze the electroless Ni plating in a sodium hypophosphite bath, it was necessary to first activate the copper substrate. Typically, copper is sensitized using Sn(II) and then activated with Pd(II). Feldstein *et al.*[11] suggested a one-step activation method for metal or alloy (*e.g.*, Cu) substrates by depositing small amounts of Ni onto the metal substrate using a Ni-DMAB developer solution. The reaction involved Cu-catalyzed reduction of Ni^{2+} by DMAB. The resulting Ni layer further catalyzed the reduction of the Ni in a Ni-P bath. The development step required a higher temperature (~40°C) and a Ni-DMAB developer solution. To simplify the procedure, we made use of only a 2-g/L DMAB solution in water at room temperature. The LCC substrate was soaked in 10% H_2SO_4 solution for 10 min to remove any rust or oxide, and thereafter, we rinsed and soaked the substrate in 2 g/L DMAB solution for 30 min. After this step, the activated surface was dipped into the appropriate bath to initiate electroless plating. On copper surface, Ni(II) was reduced into metal Ni by DMAB with Cu acting as the catalyst and the deposited Ni further catalyzed the reduction of Ni(II) by sodium hypophosphite in the Ni-P baths.

Elemental composition and FTIR analysis.—Energy dispersive spectrometry (EDS) was conducted to investigate the composition of the plated Ni film. EDS was performed using a Princeton Gamma-Tech IMIX X-ray microanalysis system (NJ). Fourier transform infrared (FTIR) analysis was determined with a Nicolet Magna-IR 760 spectrometer (Madison, WI) using Kapton substrate because the Ni was easier to strip off using this substrate. The Kapton was sensitized in a similar manner as the LCC before being soaked in Ni bath for 2 min. The substrates were dried and the plated Ni layers stripped off, mixed with KBr and pressed to a pellet for FTIR analysis.

QCM.—The plating of Ni onto a QCM was achieved using the QCM setup that was described above. In this setup, a layer of Ni was electroplated onto the gold surface of the QCM, and the whole QCM cell was immersed into the electroless Ni plating solution at 80°C. The increase in mass (or frequency decrease) was recorded using the QCM analyzer. The plating time was 10 s for each bath composition.

Gravimetric analysis.—The determination of the microscopic mass using QCM was correlated with classical gravimetric techniques. An LCC sample was first weighed, and then soaked in a 10% H_2SO_4 solution to remove oxide or rust. This was further rinsed using DI water before being immersed into the plating solution. The sample was not dried nor weighed before immersion into the plating solution to avoid the formation of oxide. After plating, the sample was rinsed, dried, and then weighed to estimate the mass of Ni plated. The exact plating rate was obtained by measuring the thickness of the Ni that was plated using X-ray fluorescence spectroscopy (XRF).

X-ray fluorescence spectroscopy.—The thickness of the plated Ni was measured using Fisherscope X-ray system XDVM (Fisher Technology, Windsor, CT). The sample was positioned under the locating light and the thickness was measured by the software-controlled system.

Results and Discussion

In acidic medium electroless Ni plating involves the reduction of free Ni^{2+} and $Ni(Ac)_2$ (when HAc was used as the complexing agent), as well as the oxidation of hypophosphite in which the latter step was considered as rate determining.[12] These steps can be represented as follows

$$2H_2PO_2^- + 2H_2O \rightarrow 2H_2PO_3^- + 2H^+ + 2H^- \qquad [1]$$

$$Ni^{2+} + 2H^- \rightarrow Ni + H_2 \qquad [2]$$

$$Ni(Ac)_2 + 2H^- \rightarrow Ni + H_2 + 2Ac^- \qquad [2']$$

Thus the overall Ni plating reaction in acidic condition is often represented as

$$Ni^{2+} + 2H_2PO_2^- + 2H_2O \rightarrow Ni\ (\text{metallic}) + 2H_2PO_3^- + 2H^+ + H_2 \qquad [3]$$

$$Ni(Ac)_2 + 2H_2PO_2^- + 2H_2O \rightarrow Ni\ (\text{metallic}) + 2H_2PO_3^- + 2H^+ + H_2 + 2Ac^- \qquad [3']$$

Plating is accompanied by an obvious production of hydrogen gas, which may be inhibited through the addition of stabilizer (such as thiourea). In that case, the stabilizer could be adsorbed onto the surface of the substrate. This could decrease the number of catalytic sites and depress the hydrogenation/dehydrogenation catalysis.[12] This would inherently decrease the plating rate and subsequently

Table III. Composition and operating conditions for nickel hypophosphite bath at variable reducing agents' concentrations.[a]

Bath constituents	g/L
$NiSO_4 \cdot 7H_2O$	6.0
$NaH_2PO_2 \cdot H_2O$	Variable (5-50)
Thiourea	0.05 ppm
Acetic acid	30.0
pH	5.1
Bath Temperature	82°C

[a] No plating was recorded when lead acetate was used as bath stabilizer.

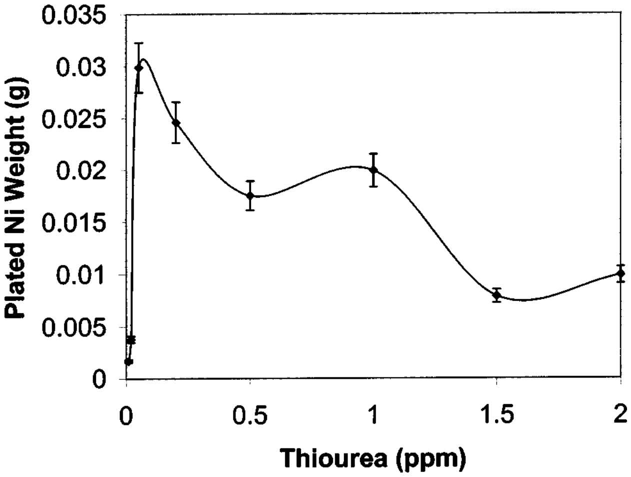


Figure 1. The effect of thiourea on bath chemistry using gravimetry bath compositions (Table I). LCC Cu as the substrates, plating time: 30 min.

stabilize the plating bath. We have studied the effect of stabilizing agents, thiourea, and lead acetate using classical gravimetry and QCM techniques.

Effect of stabilizing agent on plating.—Typical stabilizers used in Ni baths include Group IV elements (*e.g.*, Se, Te), oxygen-containing compounds (*e.g.*, AsO_2^-) and unsaturated organic compounds (*e.g.*, thiourea and metal ions such as Pb^{2+}). The first two stabilizer types are more toxic than the latter two. For this reason, we used only thiourea and lead acetate in our experiments. It was found that when lead acetate was used as the stabilizing agent, the plating of Ni was almost completely inhibited, even at 0.01 ppm lead acetate. Only a small portion of the LCC sample was plated. So, in the baths containing HAc as the complexing agents and sodium hypophosphite as the reducing agents, lead acetate was found to completely inhibit the plating. Therefore, this leads to our conclusion that lead acetate could not be used as stabilizer in the current bath composition and should be avoided to eliminate any contamination.

Thiourea can be strongly adsorbed onto catalytic surfaces.[13,14] Solution agitation in the presence of the stabilizer can cause inhibition of the nickel deposition reaction, which can be noticeable by a decrease in the plating rate. As stated earlier, when the stabilizer is adsorbed onto the catalytic surface, the number of catalytic sites available for dehydrogenation of hypophosphite is reduced. Complexing agents are also required to decrease the concentration of free metal ions such as Ni(II) and hence the deposition rate.

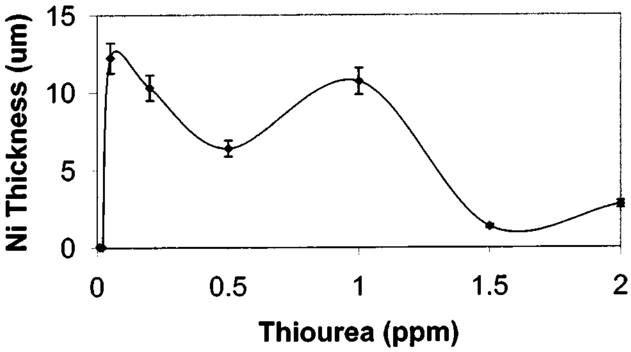


Figure 2. The effect of thiourea on thickness of Ni deposit using XRF. Bath compositions and conditions as in Fig. 1.

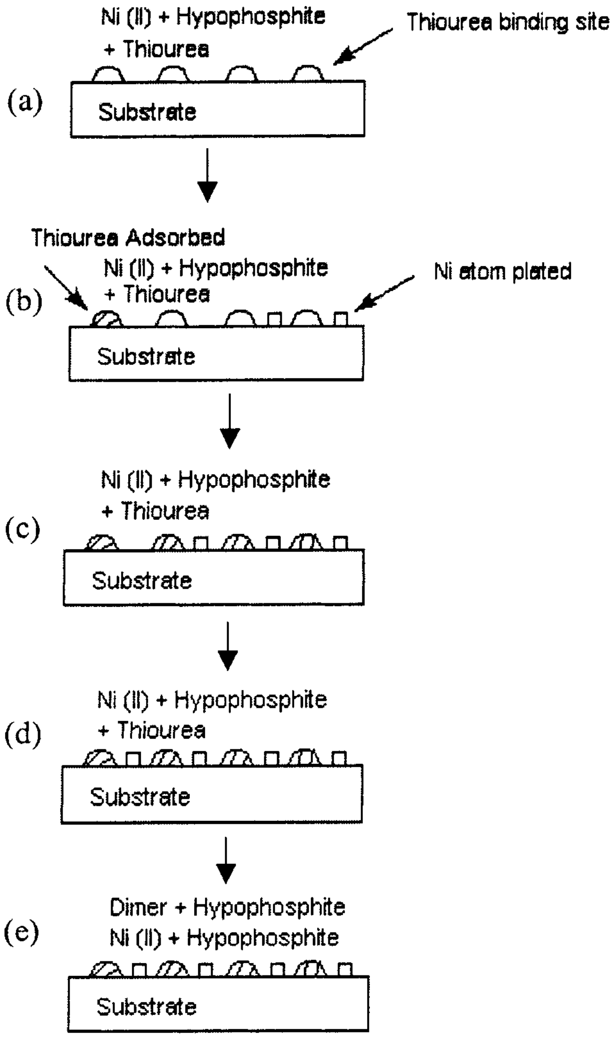
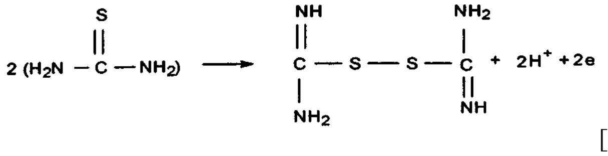


Figure 3. The condition of the substrate surface as thiourea was added to the plating bath during electroless deposition of nickel. (a) Thiourea binding sites on the surface. (b) Catalysis process was dominant on the surface to increase the plating rate. (c) The adsorption of thiourea was predominant to increase the plating rate resulting in the first maximum plating rate. (d) Catalysis process was predominant again to increase the plating rate. (e) Competing process occurring between the thiourea dimer and Ni^{2+} for hypophosphite, which decreased the plating rate resulting in the second maximum plating rate.

We first utilized the weight gain method to determine the plating efficiency of the baths as shown in Tables I, II, and III. Using the classical gravimetric techniques, the weight gained recorded at each LCC substrate using different thiourea concentration is shown in Fig. 1. Two maxima were observed in Fig. 1. The first occurred at a thiourea concentration of 0.05 ppm, while the second was noticed at 1 ppm thiourea concentration. This suggested that the weight gain method could also be used to predict the plating rates. To our knowledge, this appears to be the first time a bimodal distribution was recorded for stabilizer concentration. Our observation was consistent with the phenomenon reported earlier in which thiourea was first suggested to increase the plating rate at very low concentration but subsequently decreased the plating rate.[15] Perhaps, the levels of stabilizer concentrations studied in previous reports could have been very high, which might have prevented the observation of the bimodal distribution recorded in this work.[5-7] This rather unexpected finding has prompted us to conduct a detailed, systematic study of the role of different bath species to plating efficiency. The gravimetry analysis was correlated to the thickness effects using XRF. As shown in Fig. 2, the thickness measured using XRF followed a similar trend as with the gravimetry when thiourea concentration was varied. The complicated bimodal distribution shown in Fig. 1

and 2, which related the plating rate to the concentration of thiourea could be explained using the following mechanism.

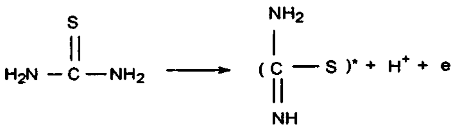
Mechanism of stabilizer regeneration at electroless nickel baths.—According to the proposed mechanism, thiourea was first oxidized into a reactive intermediate radical, which facilitated the transfer of electrons to the Ni ions. It is this anodic reaction that inherently accelerated the plating rate, yielding elemental Ni and formamidine disulfide. The formamidine disulfide was then reduced by hypophosphite to regenerate the thiourea. The elementary steps involved in this mechanism are described from Eq. 4 through 8



$$2\,(H_2N-C(=S)-NH_2) \longrightarrow HN{=}C(NH_2)-S-S-C(NH_2){=}NH + 2H^+ + 2e \quad [4]$$

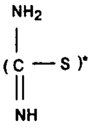
The oxidation of thiourea follows a two-step mechanism in which the tautomeric form of thiourea is oxidized to a thiourea free radical (Thiourea*) through a charge transfer.[16a] The thiourea* will likely react with another radical to form reactive intermediate disulfide. This process produces a reversible mechanism that regenerates the thiourea

- Thiourea = thiourea* + H^+ + e



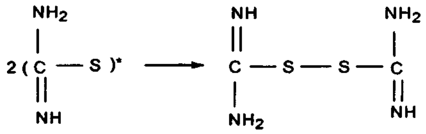
$$H_2N-C(=S)-NH_2 \longrightarrow (C(NH_2)(=NH)-S)^{\bullet} + H^+ + e \quad [5]$$

- where thiourea* =



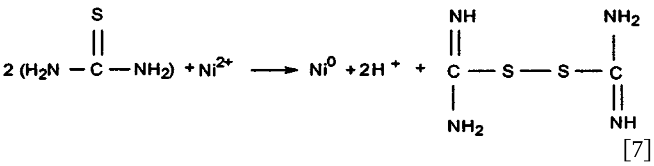
$$(C(NH_2)(=NH)-S)^{\bullet}$$

- Then, 2 thiourea* → formamidine disulfide



$$2\,(C(NH_2)(=NH)-S)^{\bullet} \longrightarrow HN{=}C(NH_2)-S-S-C(NH_2){=}NH \quad [6]$$

- The overall reaction with Ni^{2+} and $H_2PO_3^-$ will be



$$2\,(H_2N-C(=S)-NH_2) + Ni^{2+} \longrightarrow Ni^0 + 2H^+ + HN{=}C(NH_2)-S-S-C(NH_2){=}NH \quad [7]$$

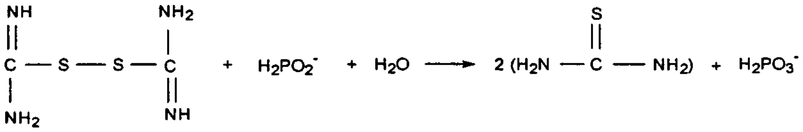
- The dimer produced is finally reduced by $H_2PO_2^-$ as in Eq. 8. Thus, Thiourea is regenerated following a reduction of formamidine disulfide by hypophosphite. It seems highly probable that the reduction of formamidine disulfide may also proceed via a breakdown product into two thiourea free radicals, which are then subsequently reduced to thiourea. The radical formation in Eq. 5 is reasonable intermediate for a single electron oxidation process because the end product is a disulfide.[16] The presence of the radical formation from thiourea has been confirmed by chemical oxidation by hydrogen peroxide using electron spin resonance.[17]

On the other hand, a competing mechanism may predominate in which the thiourea is adsorbed onto the substrate surface where it impedes the plating reaction as illustrated in Fig. 3a. We believe that when small amount of thiourea is added to the bath solution, the plating rate increases because the former processes (the catalysis process, Eq. 4-8) are predominant as in Fig. 3b and part a of Fig. 4. When additional thiourea ($>$0.05 ppm) was added, more of Tu adsorbed onto the substrate surface. This decreased the number of active sites and slowed the plating rates. This explains the maximum plating rate observed at 0.05 ppm. With continuous addition of thiourea, more thiourea would adsorb onto the substrate surface and would further decrease the plating rate until all available thiourea binding sites are filled and the plating rate reaches a minimum as illustrated in Fig. 3c and part b of Fig. 4. When an increasing amount of thiourea was added, the plating rate increased again because no more thiourea could adsorb onto the substrate surface (all available binding sites have been filled) to decrease the plating rate, and the catalytic process (Eq. 3.4-3.8) would be predominant again to increase the plating rate as illustrated in Fig. 3d and part c of Fig. 4. As additional thiourea was added, more formamidine disulfide was produced, and when that dimer had been generated in sufficient amount, its ability to oxidize $H_2PO_3^-$ to $H_3PO_3^-$ (Eq. 8) inhibited the reduction of Ni^{2+} by $H_2PO_3^-$ thus decreasing the Ni deposition rate. So, with the competing effect of thiourea, the second maximum plating rate resulted at 1 ppm thiourea resulted and the rate continued to decrease with more thiourea added as illustrated in Fig. 3e and part d of Fig. 4.

A QCM study was then conducted to validate the results obtained using the weight gain method. In QCM, the mass of a metal or other substance deposited onto the quartz electrode can be related to the change in frequency by using Saurbrey equation[18]

$$\Delta f = -\left(\frac{2f_0^2}{S\sqrt{\mu\rho}}\right)\Delta m \quad [9]$$

where Δf is the change in frequency of the crystal (which is a measurable parameter), f_0 is the fundamental resonant frequency of the crystal (in the electrolyte), S is the electrode area, μ is the sheer modulus of the crystal (2.947×10^{11} g cm^{-1} s^{-2}), ρ is the density of the quartz (2.648 g cm^{-3}), and Δm is the change in mass at the surface of the crystal resonator. Therefore, the adsorption/desorption processes at the electrode surface can be monitored as a function of the change in mass.



$$HN{=}C(NH_2)-S-S-C(NH_2){=}NH + H_2PO_2^- + H_2O \longrightarrow 2\,(H_2N-C(=S)-NH_2) + H_2PO_3^- \quad [8]$$

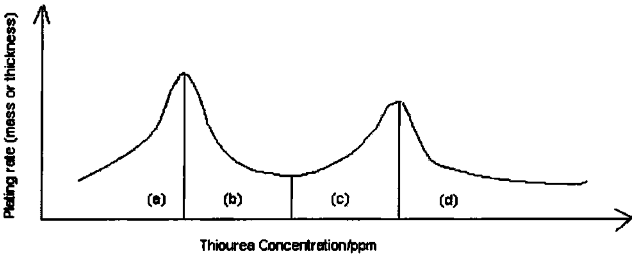


Figure 4. The dependence of plating rate on thiourea. (a) Rate increased with thiourea where the catalytic process is predominant. (b) Rate decreased where the adsorption of thiourea onto the surface is predominant; (c) Rate increased again where the catalytic process was predominant and no available binding site thiourea. (d) Rate decreased due to the competition between the dimer and Ni(II) for hypophosphite.

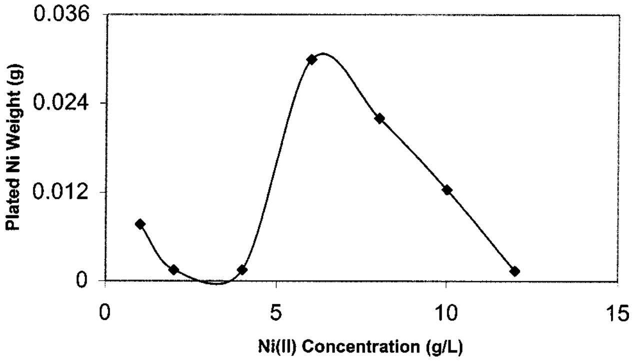


Figure 6. The effect of Ni(II) on bath chemistry using gravimetric technique (Table II). LCC Cu was used as the substrates with plating time of 30 min.

The increase in mass *vs.* thiourea concentration when Ni was electrolessly plated onto the QCM is shown in Fig. 5. This result showed that the relationship obtained from QCM was the same as that generated using classical gravimetry. This further supports our mechanism described above. Additional experiments were performed to better understand the effect of Ni(II) or sodium hypophosphite on plating efficiency. The results shown in Fig. 1, 2, and 5 indicate that the plating rate is higher when thiourea concentration is kept at 0.05 ppm. However, for practical purposes, we decided to use Ni plating bath having thiourea concentration of 1 ppm because noticeable fluctuation in the plating rates are recorded at thiourea concentration of 0.05 ppm, which makes the plating unstable.

The effect of Ni(II) on electroless Ni plating.—We studied the effect of changing the concentration of Ni(II) on plating rate by varying its concentration while keeping other parameters constant (Table II). The effect of Ni(II) concentration on the deposition rate is shown in Fig. 6 using weight gain method and XRF techniques. Because both the weight gain method and XRF technique exhibited similar tendency, subsequent results were reported using only the weight gain method. It can be observed that the highest plating rate was recorded between 4 to 6 g/L (Fig. 6). It was also noted that at Ni(II) concentration of 4 g/L, partial and uneven plating was observed on the LCC substrate. However, at increasingly higher concentration of Ni(II), especially at 10 g/L Ni concentration, the deposition rate was quite high such that the bath began to decompose. This was evident by the rapid decay in the plating rate beyond 6 g/L. Therefore at extremely high Ni(II) concentration (12 g/L), the bath rapidly decomposed because excess free Ni(II) was present that could not be complexed by the HAc ligand. This corresponds to the processes occurring in Eq. 2-3′. Because the reduction of Ni(II) was too fast, we observed that the LCC samples were not plated. So, it was concluded that the critical concentration required for Ni(II) in this bath was 6 g/L. Subsequently, the effect of hypophosphite was studied using the established concentration.

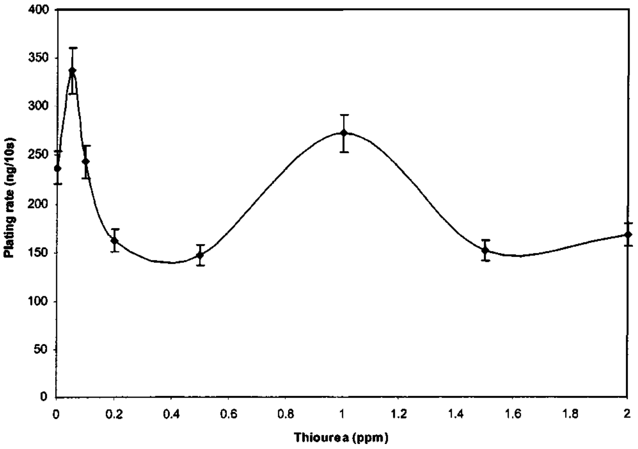


Figure 5. The effect of thiourea on the mass increase of the QCM immersed in the Ni plating solution. Bath compositions and conditions as in Fig. 1 while the plating time was 10 s.

The effect of sodium hypophosphite on electroless Ni plating.—The effect of sodium hypophosphite was studied using the composition shown in Table III. By varying the concentration of sodium hypophosphite, we expected that the plating rate for the Ni bath would change. Figure 7 shows the weight gain of Ni at varying hypophosphite concentrations. Results indicated that as the concentration of sodium hypophosphite increased, the plating rate also increased, but later leveled off at 30 g/L sodium hypophosphite. The effect of sodium hypophosphite on Ni plating was not as dramatic as when Ni or thiourea concentrations were varied.

EDX analysis and FTIR studies.—The elemental composition of the electroless nickel layer was investigated using EDX and FTIR techniques. A representative EDX spectrum is shown in Fig. 8. The strong Ni peaks at 0.05 and 0.10 ppm thiourea were located at approximately 7.5 keV. Another weak Ni peak was observed at 1.0 keV. Phosphorus peaks were observed at 2.0 keV, which signified the inclusion of either elemental phosphorus or hypophosphite anion in the plated Ni layer. The EDX spectrum also confirmed that the deposited Ni peaks were pure Ni phases. The ratio of Ni:P found also examined. At less than 0.05 ppm Tu, the proportion of Ni (7.5 keV) to phosphorus (12.0 keV) was determined to be ~6.3. This proportion however increased to 7.3 when Tu concentration changed to 1 ppm. This is attributed to the relative increase in the amount of Ni.

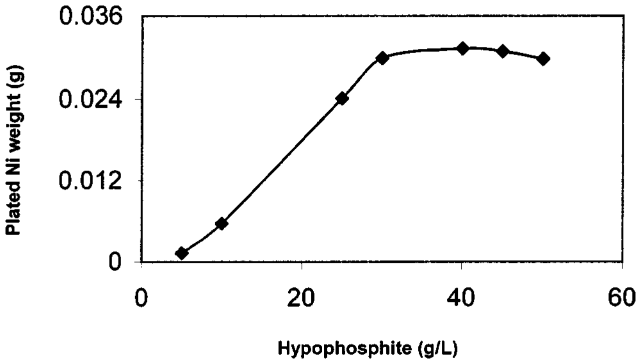


Figure 7. The effect of NaH_2PO_2 on bath chemistry using gravimetry (Table III). Other conditions as in Fig. 4.

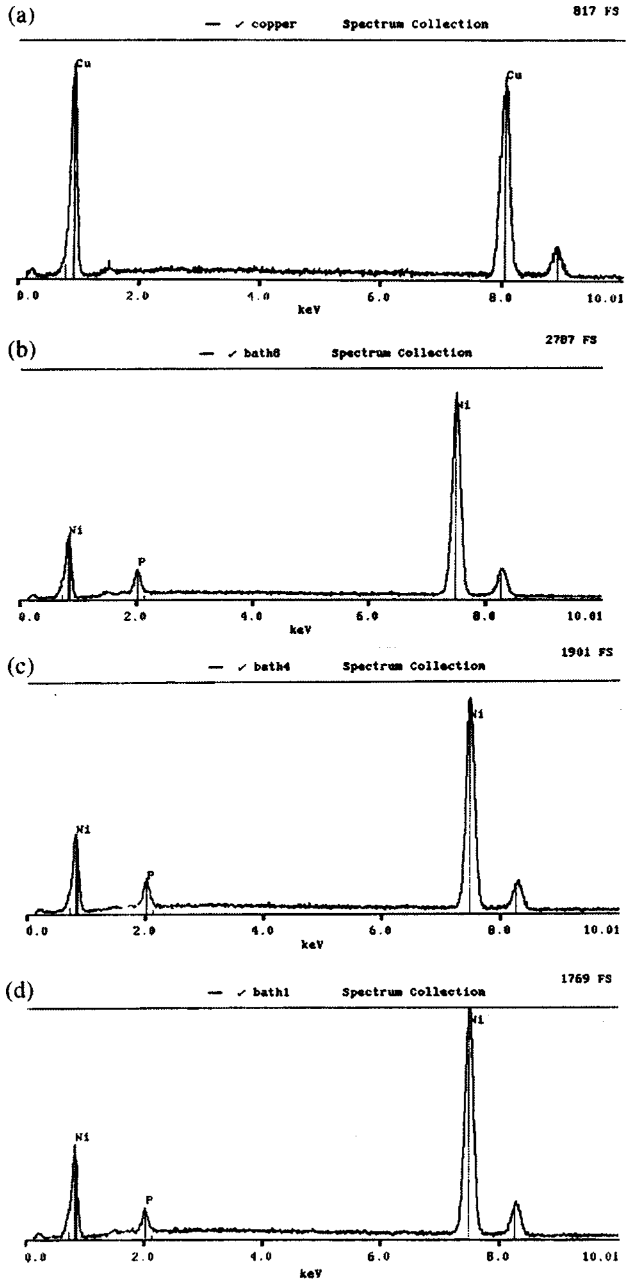


Figure 8. EDX spectra recorded for plated Ni samples at varying concentrations of thiourea. Bath compositions include: Ni(II) at 6 g/L, $NaH_2PO_2 \cdot H_2O$ at 30 g/L, HAc at 30 g/L, pH = 5.1. Temperature 82°C, plating time was 30 min and thiourea concentrations at (a) bare copper substrate, (b) 0.01, (c) 0.05 ppm, and (d) 1 ppm.

Moreover, the EDX spectra qualitatively revealed a higher proportion of Ni to P at very high Tu concentration. It could be assumed that metallic Ni was codeposited with elemental P to form an Ni-P layer but there was no codeposition of sulfur. The absence of sulfur peaks in the EDX study regardless of the thiourea concentration further confirmed our mechanism above. It appeared that stabilizer was regenerated. Finally, the presence of the stabilizer was examined using FTIR. The rationale is that if thiourea was incorporated in the nickel layer, certain components of these compounds (*e.g.*, sulfur) or its traces could be observed from elemental analysis. The FTIR spectra were recorded with and without thiourea present. No sulfur peaks were observed (supplementary results, Fig. 9). This could either be attributed to insufficient sensitivity of the instrument for the low levels of sulfur present or that because the Tu is regenerated, no traces could be detected. Confirmatory evidence resulting from both the EDX and FTIR however, suggests that the latter seems to be the case. The thiourea is being regenerated. Thus the optimal conditions for an acidic electroless Ni plating bath was determined to be: Ni(II), 6 g/L; sodium hypophosphite, 30 g/L; acetic acid, 30 g/L; and thiourea, 1 ppm.

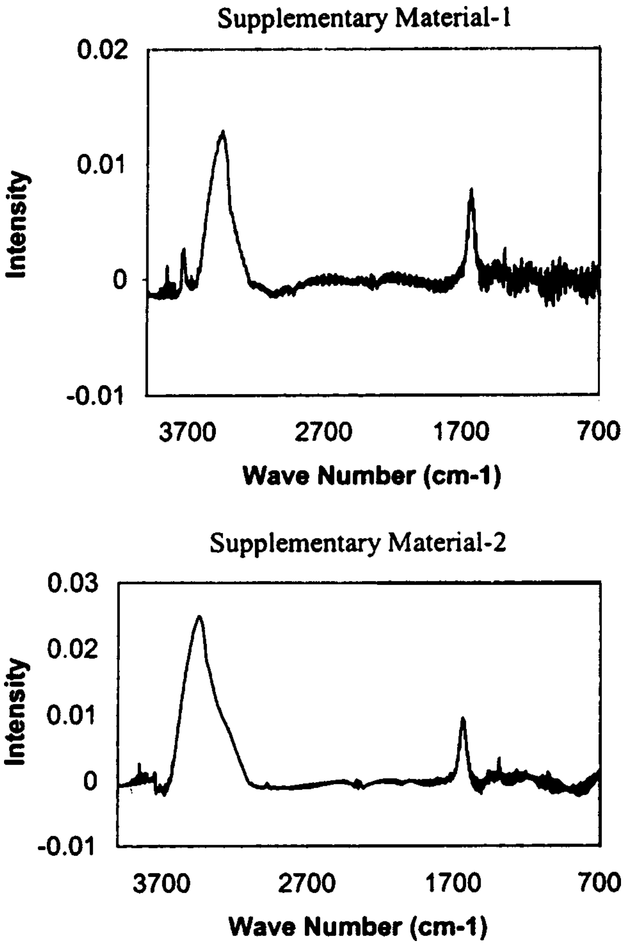


Figure 9. Experimental conditions: Supplementary material 1 shows the FTIR of the electroless Ni plated from a Ni bath without thiourea. Supplementary material 2 shows that of Ni plated from a Ni bath with 1 ppm thiourea present. Plating was achieved on Kapton substrates for FTIR experiments. The Kapton substrates were sensitized by $SnCl_2$ solution and activated using $PdCl_2$ solution (Ref. 1a) and then soaked into the two Ni baths separately for 2 min. One bath contained no thiourea while the other contained 1 ppm thiourea. Other bath compositions and conditions are as in Fig. 1.

Conclusions

We have investigated the effect of Ni(II) (as Ni source), sodium hypophosphite (as the reducing agent), thiourea, and lead acetate (both as stabilizing agents) on the electroless nickel plating. Since lead acetate was found to completely inhibit the plating reaction, we have concluded that lead acetate should be avoided in this type of bath. However, thiourea had a profound effect on the Ni plating. A bimodal distribution was observed as thiourea concentrations were varied. Therefore, a regeneration mechanism was observed for thiourea concentration and this was confirmed using EDX and FTIR data. Thus the optimal conditions for the acidic electroless Ni plating bath was determined to be Ni(II) at 6 g/L; sodium hypophosphite, 30 g/L; acetic acid, 30 g/L and thiourea, 1 ppm.

Acknowledgments

The authors gratefully acknowledge financial support from the Integrated Electronics and Electrical Center (IEEC) at SUNY-Binghamton. J.B. is also grateful for his NIH-funded Bridge-to-Baccalaureate Program at SUNY-Binghamton. We also acknowledge Anita Sargent of IBM Microelectronics, Endicott, NY, for providing the wirebond Cu samples and for performing XRF thickness measurements and finally, Bill Blackburn of Geology Department is acknowledged for performing the EDX measurements.

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