

Probing the Mechanism of Electroless Gold Plating Using an EQCM

II. Effect of Bath Additives on Interfacial Plating Processes

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This work describes results of a mechanistic investigation of electroless gold plating from a dimethylamine borane (DMAB) bath, which was performed with the aid of the electrochemical quartz crystal microbalance (EQCM). It was found that the interaction of DMAB with the gold surface during deposition is dependent on bath composition. The extent, or strength, of this interaction is detected as an anodic current increase coinciding with a mass increase at the gold surface on the cathodic scan in the vicinity of the gold oxide reduction potential. Electrochemical impedance spectroscopy of a gold electrode in DMAB solutions shows a decrease in double-layer capacitance (C_{dl}) with an increase in DMAB concentration at the reactivation potential, suggesting a strong concentration-dependent binding capacity upon gold oxide reduction. The C_{dl} reaches a limiting value at approximately 1 g/L, implying that sufficient reactive intermediate is formed at this concentration, which binds to all available free gold sites upon gold oxide reduction. Measurements of the plating rate using EQCM on industrial end-of-line wirebond monitors showed that an increase in plating rate is associated with a greater extent of interaction between the reducing agent and the catalytic gold surface. These results were confirmed with X-ray fluorescence, scanning electron microscopy, and energy-dispersive spectrophotometry. The usefulness of the EQCM as a screening tool to predict electroless gold plating rates in baths of varying formulation is presented. This technique may be applicable to other electroless baths where interfacial adsorption/desorption processes are expected to play an important role during deposition.

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Electroless gold is widely used in electronic packaging applications due to its low contact resistance, high purity, and high resistance to oxide formation.¹⁻¹⁰ Understanding the plating chemistry is a major challenge in the use of electroless plating for certain applications, such as plating through high aspect ratio holes and wirebonding applications. Although the purity, softness, and thickness of the electroless gold finish for wirebonding applications is essential for durable chip-to-carrier interconnects, the deposit quality is greatly influenced by bath chemistry.^{9,10} Therefore, understanding the bath chemistry enables the manipulation of bath parameters for enhanced plating efficiency.

In Part I, we described the interaction of a reactive, boroncontaining intermediate from dimethylamine borane (DMAB) solutions with the gold surface upon gold oxide reduction.¹¹ It is believed that following gold oxide reduction, free Au sites are available for complexation with the reactive intermediate causing an activation of DMAB oxidation at the "reactivation" potential. The extent of interaction was found to depend directly on DMAB concentration and possible boron-containing reactive intermediates. We found that in an actual electroless gold plating bath containing DMAB as reducing agent, the interaction of the reactive intermediate is not significantly inhibited by the presence of cyanide, which tends to oppose the plating reaction by inducing gold dissolution. Therefore, the feasibility of using the electrochemical quartz crystal microbalance (EQCM) to detect the interaction of the reactive intermediate with the catalytic gold surface during plating was demonstrated.

The unique ability of the EQCM to detect the interaction of the reducing agent DMAB with the gold surface prompted further investigation into the possibility of using the EQCM as a screening tool to predict the relative plating rates of electroless gold baths containing various additives. Specifically, the effect of certain additives on the interfacial behavior of the reactive intermediate may directly influence the plating rate. In this study, the effect of sulfanilic acid, chloride ion, 1,5-naphthalenedisulfonic acid, and hydro-quinonesulfonic acid on the extent of interaction between the reac-

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tive intermediate and the gold surface is investigated by EQCM. The mass increase detected for ten different bath formulations is correlated to plating rates obtained on industrial laminate chip carrier (LCC) wirebond samples.

Experimental

Materials.—Potassium hydroxide (99.9%, semiconductor grade), potassium cyanide, sodium chloride, 1,5-naphthalenedisulfonic acid tetrahydrate, sulfanilic acid, and hydroquinonesulfonic acid were obtained from Aldrich chemicals. Dimethylamine borane (97%) and KAu(CN)₂ were obtained from Alpha Aesar. All solutions were prepared with Nanopure deionized water with a resistivity of 17.5 M Ω cm.

Double-layer capacitance measurements.—Electrochemical impedance measurements were obtained with the use of an EG&G model 5210 lock-in amplifier connected to an EG&G model 263A potentiostat. A gold disk (BAS, 0.02 cm²) was used as the working electrode. Ag/AgCl and Pt gauze were used as the reference and counter electrodes, respectively. The solution was stirred using a Thermolyne stirrer at 50% full scale to avoid concentration polarization and establish mass transport-limited conditions. Stock DMAB solution (20 g/L) was added to 100 mL of the base electrolyte (40 g/L KOH) to increase the total concentration of DMAB in the cell without disturbing the working electrode. Following each addition of DMAB, the cell was allowed to equilibrate at the bias potential for 2 min prior to running the impedance measurement. Impedance spectra were recorded within the range 100 kHz to 100 mHz with an amplitude of 5 mV at a bias potential of 0.184 V. The bias potential was the reactivation potential at gold oxide reduction selected from a prior cyclic voltammogram (CV) test run under stationary conditions. C_{dl} at each DMAB concentration was extracted from the x intercept of the capacitance Z'' vs. Z' plot.

Electroless gold plating of laminate chip carrier (wirebond) samples.—Ten LCCs were plated with the electroless gold compositions shown in Table I. The LCCs act as wirebond samples for wirebond testing at end-of-line processing. The chip carriers were provided by IBM Microelectronics in Endicott, NY. Prior to receipt in our laboratory, the LCC were circuitized with copper, followed by metallization with electroless nickel (115 μ in.) and immersion

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Bath 1		Bath 2		Bath 3		Bath 4		Bath 5	
Component	(g/L)	Component	(g/L)	Component	(g/L)	Component	(g/L)	Component	(g/L)
КОН	40	КОН	40	КОН	40	КОН	40	КОН	4
DMAB	5	DMAB	2.5	DMAB	10	DMAB	5	DMAB	5
KCN	2.1	KCN	2.1	KCN	2.1	KCN	1.05	KCN	2.1
KAu(CN) ₂	3	KAu(CN) ₂	3	KAu(CN) ₂	3	KAu(CN) ₂	3	KAu(CN) ₂	3
Bath 6		Bath 7		Bath 8		Bath 9		Bath 10	
Component	(g/L)	Component	(g/L)	Component	(g/L)	Component	(g/L)	Component	(g/L)
КОН	40	КОН	40	КОН	40	КОН	40	КОН	40
DMAB	5	DMAB	5	DMAB	5	DMAB	5	DMAB	5
KCN	2.1	KCN	2.1	KCN	2.1	KCN	2.1	KCN	2.1
KAu(CN) ₂	1.5	KAu(CN) ₂	3	KAu(CN) ₂	3	KAu(CN) ₂	3	KAu(CN) ₂	3
		sulfanilic acid	0.1	NaCl	5.84	1,5-naphthalene- sulfonic acid	1	hydroquinone- sulfonic acid	1

Table I. Plating conditions for wirebond samples.

gold (3 µin.). Electroless gold plating was then performed under moderate stirring conditions at 70°C in a polypropylene beaker to minimize contamination from etched glass. Total bath volume was 500 mL. Each substrate (LCC, 2.5×2.5 cm) was immersed in the electroless gold bath 10 min after addition of reducing agent. After 15 min of plating time, a 500 μ L aliquot of the bath was placed into a well-type Teflon-based EQCM measurement cell and allowed to cool to room temperature. The working electrode consisted of 0.196 cm^2 gold (3000 Å) sputtered onto a titanium layer (500 Å) on a quartz crystal base having a frequency of 9 MHz. Ag/AgCl and Pt were used as the reference and counter electrodes, respectively. Each gold working electrode surface was precleaned by immersion in piranha solution (3:1 v/v concentrated sulfuric acid: 30% hydrogen peroxide) for 20 min. The gold surfaces were then thoroughly rinsed with deionized water, and subsequently dried under a gentle stream of nitrogen. The simultaneous current-potential (I-E) and frequency changes were recorded with an EG&G model 263A potentiostat coupled to a Seiko/EG&G QCA 917 quartz crystal analyzer. Each sample was scanned for at least six cycles until the I-E and frequency response curves were reproducible.

After 45 min of plating, the wirebond samples were removed from the plating solution, thoroughly rinsed with deionized water, and dried under nitrogen. Plating thickness measurements of the electroless gold layer were obtained by X-ray fluorescence measurements using a Fisherscope X-ray System X-ray D-type versatile multiple collimator (XDVM).

Results

The DMAB-gold interface.—DMAB functions as a reducing agent by first undergoing a substitution reaction with hydroxide ions in alkaline media to form BH_3OH^- according to^{7,12,13}

$$(CH_3)_2NHBH_3 + OH^- \rightarrow BH_3OH^- + (CH_3)_2NH$$
 [1]

The overall electroless gold deposition reaction is reported as^{1,7,14,15}

$$(CH_3)_2NHBH_3 + 4 OH^- + 3Au(CN)_2^-$$

 $\rightarrow (CH_3)_2NH + BO_2^- + 3/2H_2 + 2H_2O + 3Au + 6CN^-$
[2]

The boron in BH_3OH^- has a valence of (-)3 and is able to reduce the gold dicyanide complex due to its relatively low thermodynamic standard reduction potential. This is an intermediate species that is presumed to have an important role in the gold deposition process. The exact chemical structure of this intermediate at the gold/solution interface and how it relates to the autocatalytic deposition process is still not clear.¹⁶ In this work, we refer to BH_3OH^- as the reactive intermediate. Previous work in our lab has shown that reactive intermediate adsorbs to the gold surface in the region where gold oxide is reduced.¹¹ Reduction of the passivating oxide layer allows

DMAB oxidation to resume. The potential at which the gold oxide reduces is termed the reactivation potential, since the gold surface reactivates with respect to DMAB oxidation. Since adsorption of the reactive intermediate to the gold surface may play an important role in the autocatalytic activity of the bath, it would be of interest to determine whether a concentration of DMAB exists where adsorption exhibits a saturation limit in response. The CVs and simultaneous mass changes recorded for DMAB on gold in alkaline solutions using the EQCM are shown in Fig. 1a and b, respectively. For all concentrations shown, anodic scanning yields a sizable mass loss from gold dissolution within the range -0.4 to 0 V. From 0 to 0.6 V, the formation of gold oxide on the working electrode surface results in a noticeable mass increase that terminates in a plateau. The oxide layer further inhibits the interfacial reactions such that a drop in current occurs and a plateau is reached in both the I-E and mass responses. Scanning in the reverse direction, the gold oxide layer gradually becomes reduced between 0.6 and -0.2 V, expelling adsorbed OH⁻ and causing the mass loss recorded in this potential region.

At -0.2 V, reduction of gold oxide is complete and a mass increase can be detected in the presence of DMAB. At very low DMAB concentrations, *i.e.*, 0.1 g/L, a mass increase is barely detected at the potential of gold oxide reduction. With an increase in DMAB concentration, the mass increase signifying adsorption of a reactive intermediate to the gold surface is apparent. Beyond 1 g/L, the mass increase does not change. This implies that there exists of a limited number of free Au sites with which the reactive intermediate may interact. Good reproducibility of the mass change response is shown in Fig. 2 for 0.5 g/L, with the exception of gradual gold dissolution due to continuous scanning.

Saturation of a mass change response corresponding to an increase in DMAB concentration should also exhibit a limiting $C_{\rm dl}$. Specifically, as the available Au sites become obstructed due to adsorption of reactive intermediate, additional adsorbing species settle in the outer Helmholtz plane (OHP). Beyond the OHP, the dependence of $C_{\rm dl}$ on concentration of adsorbing species becomes negligible. Therefore, a decrease in $C_{\rm dl}$ to a limiting value should be observed with increasing DMAB concentration that is consistent with the saturation in mass increase described above. One method of determining $C_{\rm dl}$ involves perturbing the electrode with a small-amplitude ac signal and observing the response over a wide frequency range, *i.e.*, electrochemical impedance spectroscopy.

Values of C_{dl} obtained from impedance plots (Z'' vs. Z') at various concentrations of DMAB on gold held at the reactivation potential (0.184 V) in alkaline solution are shown in Fig. 3. A trend toward a lower limit for C_{dl} is apparent at approximately 1 g/L DMAB. This is consistent with the saturation of mass response that is observed for DMAB on gold with an increase in concentration, and suggests that the formation and reduction of the gold oxide serves as an indirect measure of catalytic activity of DMAB on gold



Figure 1. (a) CVs of DMAB in 40 g/L KOH on gold; (i) 0.1 g/L, (ii) 0.5 g/L, (iii) 1.0 g/L and (iv) 2.0 g/L. Scan rate = 50 mV/s. (b) simultaneous mass change response recorded with the EQCM; (i) 0.1 g/L, (ii) 0.5 g/L, (iii) 1.0 g/L and (iv) 2.0 g/L. Scan rate = 50 mV/s.

in alkaline solution. With this in mind, the mass change response of the electroless gold bath of varying composition, including the effect of bath additives, was studied.

Influence of bath composition on mass change response at reactivation.—At the reactivation potential, the extent of interaction between the reactive intermediate and the gold surface can be measured as a mass increase. In Part I, it was shown that this interaction is stronger at higher DMAB concentrations. According to the deposition mechanism, an increase in plating rate is afforded by an increase in DMAB concentration. Therefore, it is feasible that other conditions favoring a higher plating rate would exhibit the same tendency for greater interaction with the gold surface. For example,



Figure 2. Mass change recorded during several potential scans for 0.1 g/L DMAB in 40 g/L KOH on gold. Scan rate = 50 mV/s.

organic compounds containing nitrogen or a π -delocalized ring structure may be added to the bath to enhance the deposition rate. It is thought that these additives interact strongly (via chemisorption) with the substrate surface or stabilize intermediates during the deposition process to increase the deposition rate. We wanted to test this possibility by recording the EQCM response for ten electroless gold baths with differing composition and correlating the mass increase at the reactivation potential with the plating rate on actual industrial wirebond monitors.

Effect of bath composition on plating rate.—Ten LCC wirebond samples having a metallization layer composed of Cu/electroless Ni/immersion Au were plated with electroless gold having the compositions shown in Table I. The electroless nickel serves as a diffusion barrier to prevent copper migration and the immersion gold serves as a preplate for a smooth catalytic surface for electroless gold deposition to take place. If electroless deposition of gold is hindered due to either insufficient concentration of reducing agent or low hydroxide content, gold cyanidation becomes a competing process, which may result in etching of the immersion gold layer.



Figure 3. Variation of $C_{\rm dl}$ with concentration of DMAB. Electrolyte = 40 g/LKOH. $C_{\rm dl}$ values are extracted from capacitance plot of impedance data.

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Bath 1 is a commonly used electroless gold formulation containing only the four essential bath components: KOH (40 g/L), DMAB as reducing agent (5 g/L), KAu(CN)₂ as gold source (3 g/L), and KCN as stabilizer (2.1 g/L). Baths 2-6 are variations of bath 1 to test the effect of these parameters on the mass changes recorded with the EQCM. Figure 4a and b are mass changes recorded for baths 1-10 during potential scanning. For bath 1, a small increase in mass is detected at the reactivation potential, as indicated by the arrow in Fig. 4a. This mass increase signifies adsorption of a reactive intermediate(s) from DMAB to the gold surface.¹¹ An inspection reveals that increasing the DMAB concentration, decreasing free cyanide, and lowering the concentration of $Au(CN)_2^-$ all yield a larger mass increase at the reactivation potential compared to the parent bath 1. This is easily explained by Eq. 2. The mass detected at reactivation increases with DMAB concentration since more reactive intermediate produced by interaction of OH⁻ with DMAB adsorbs to the gold surface. Lowering the cyanide concentration lessens the tendency for gold dissolution to proceed as an opposing reaction to deposition. This behavior can also be explained according to Eq. 2.

An increase in DMAB and a decrease in CN^- increase the plating rate, which corresponds to a greater extent of interaction between the reducing agent and the gold surface at reactivation in Fig. 4a. Counter intuitively, a decrease in Au(CN)²₂ actually increases the mass detected at reactivation. However, it is believed that Au(CN)²₂ competes with BH₃OH⁻ for active gold sites.¹³ Therefore, lowering the concentration of Au(CN)²₂ makes available additional gold sites for complexation with the reactive intermediate, and yields a higher detected mass. Bath 5 exhibits negligible mass changes throughout the entire potential window, and no mass increase is detected at reactivation. This is because the concentration of OH⁻ (here, a 1:0.7 molar ratio of DMAB:KOH) is insufficient to generate BH₃OH⁻ as indicated in Eq. 1.

EQCM responses for baths 7-10 containing additives are illustrated in Fig. 4b. The chemical structures and electroactivities of these molecules are compiled in Table II. Note that within the highly alkaline environment of the electroless gold bath, these molecules exist in the anionic form. All of these baths except for bath 10 yield a higher mass increase at reactivation than parent bath 1, as shown in Fig. 5. Baths 7 and 9 contain the additives sulfanilic acid (SA) and 1,5-naphthalenesulfonic acid (1,5-NDSA). These additives are π -delocalized rings containing sulfonic acid groups that strongly adsorb to the gold surface. The sulfonic acid group provides a source of sulfur (which is known to interact strongly with coinage metals) to the metal surface, and represents the actual electroactive species,¹⁷ which is reduced at the electrode surface.

The presence of electron-rich groups, such as -OH⁻ and -NH₂ make electroreduction of the sulfonic acid group more difficult and shift their redox potential to more negative values. Naphthalenesulfonic acids have been utilized as dopants to form tubular structures of chemically polymerized polypyrrole.¹⁸ 1,5-NDSA is used as an accelerator in the DMAB-based electroless gold bath.¹⁹ It is reported to have an $E_{1/2}$ of -0.89 vs. SCE in 0.1 M KCl with a calculated *n* value of 1.04,^{17,20} although, in our experiment, no significant electroactivity of 1,5-NDSA is observed on gold in alkaline solution. This may be due to further π -delocalization owing to the high alkalinity of the electrolyte (pH \approx 13.5). Sulfanilic acid (SA) improves the smoothness of electroless Pd deposits.²¹ As shown in Table II, SA displays a redox couple at -0.6 V and an anodic peak at 0.1 V in addition to the gold oxide formation and reduction peaks normally observed. The plating rate acceleration effect caused by the additive molecules is likely due to an exchange of electrons among electrode, π -bonded additive molecule, and the complexed metal ions in the solution.²² As electron donors they are capable of stabilizing the active gold nuclei at the catalytic surface during deposition.

The presence of chloride ions in bath 8 also increases the detected mass compared to the parent bath. This is attributed to the formation of soluble gold chloride compounds, which may actively



Figure 4. Mass changes recorded during potential scans for (a) baths 1-6 and (b) baths 7-10. Scan rate = 50 mV/s.

participate in the generation of active gold sites. Overall, baths containing these additives exhibit an increase in mass detected at reactivation. An exception to this tendency is bath 10, which contains hydroquinonesulfonic acid (HQSA) as an additive. Hydroquinone



E vs Ag/AgCl (V)

Table II. Chemical structures and electroactivities of electroless gold bath additives.

itself is a colored species that has been used as a reduction promoter for electroless gold baths^{23,24} and as an antioxidant for reducing undesirable formation of tetravalent tin in tin electroplating baths. HQSA was chosen as an additive for this bath because it is a reducing agent and the sulfonic acid moiety has been known to enhance plating rates.¹⁹ The ability of hydroquinonesulfonate to mediate electron transfer in polypyrrole-based glucose oxidase sensors has been described in the literature.²⁶ Previous studies indicate that HQSA exhibits an $E_{p/2}$ of 0.42 in 0.5 M NaClO₄²⁰ with n = 2. Table II shows that it undergoes oxidation at 0.1 \vec{V} in alkaline solution. However, unlike SA and 1,5-NDSA, it does not generate a mass increase at the reactivation potential. This can be explained on the basis that HQSA is the sole reducing agent amongst the three additives selected for the study. At applied potentials greater than 0.1 V, HQSA exists in its oxidized form. Therefore, during gold

oxide reduction only the oxidized form of HQSA resides at the electrode surface within the double layer. With DMAB present, HQSA will oxidize BH₃OH⁻ at the reactivation potential, causing BH₃OH⁻ to lose electron density thereby impeding the ability of the intermediate to interact with the gold surface. To test this possibility, the influence of HQSA on the mass response was recorded in hydroxide electrolyte without DMAB present. As shown in Fig. 6, HQSA does exhibit the tendency to interact with the gold surface at reactivation, yielding a mass increase. Therefore, in the presence of DMAB, the oxidizing power of HQSA is directed toward the reactive intermediate and not to the gold surface. The electrochemical behavior of HQSA on gold in alkaline media suggests that HQSA in the electroless bath would diminish the interaction between the reactive intermediate and the gold surface, thereby eliminating the mass increase normally detected at the reactivation potential. This does not adversely affect plating, however. The mixed potential of

Evs Ag/AgCI (V)



Figure 5. Mass change at reactivation peak recorded by EQCM for baths 1-10. Scan rate = 50 mV/s.



Figure 6. (a) I-E and (b) mass change response of 8.5×10^{-4} M hydroquinonesulfonic acid in 40 g/L KOH. Scan rate = 50 mV/s.

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Figure 7. Plating rates obtained for wirebond samples in baths 1-10. Conditions for plating: 45 min at 70°C under moderate agitation.

the bath is maintained without externally applied potential, which is necessary for electrochemical techniques like cyclic voltammetry. For the DMAB-based electroless gold bath, $E_{\rm mix}$ is generally between -0.734 and -0.690 mV; therefore, at these potentials, HQSA exists only in its reduced form and further contributes to the gold deposition process.

To correlate the mass increase at reactivation with the actual plating rates obtained for different bath formulations, the plating rates for electroless gold-plated wirebond samples 1-10 were measured by X-ray fluorescence and are compiled in Fig. 7. The highest plating rates were obtained with baths 3, 6, 8, 9, and 10. The low hydroxide bath did not plate; instead, the existing immersion gold was etched by the cyanide in solution. Although no mass response was observed at the reactivation potential for HQSA in bath 10, acceleration of the plating rate over the parent bath 1 by a factor of 2 was observed. Figure 8 is a series of CVs of the baths containing additives. Most of the baths containing additive yield similar I-E behavior as bath 1 (no additive). The only difference appears to be the ability of the additive to increase the mass detected at reactivation. On the other hand, the bath containing HQSA forms the gold oxide layer with more difficulty, *i.e.*, at more anodic potentials than the others, though the reactivation current is observed at nearly the same potential.









Figure 9. SEM of wirebond pad edge (1000 times magnification) (a) before and (b) after electroless gold plate.

A possible explanation for this unique behavior is that the reduced form of HQSA maintains the surface Au nuclei in the uncharged state during the beginning of the voltammetric scan, *i.e.*, from -1.2 to 0.1 V. Because gold is normally active within the potential range -0.6 to 0 V (due to formation of premonolayer oxide) it could be that HQSA interrupts the generation of these sites at the negative potentials which are subsequently necessary for the Au(I) and Au(III) transitions. It appears that the acceleration of electroless gold deposition proceeds through a different pathway with HQSA than with chloride or the nitrogen-containing, π -delocalized organic compounds. Specifically, the HQSA may primarily act as a reduction promoter to reduce the oxidized form B(OH)₄⁻ of the



Figure 10. SEM of wirebond pad edge after plating with (a) low hydroxide, bath 5, (b) sulfanilic acid, bath 7, (c) chloride, bath 8, (d) 1, 5-naphthalenesulfonic acid bath 9, and (e) hydroquinonesulfonic acid, bath 10.

reactive intermediate BH_3OH^- to replenish and maintain the reducing power of the bath.

(e)

SEM of electroless gold surfaces.—Scanning electron microscopy (SEM) was performed on all wirebond samples before and after plating to elucidate the effect of bath formulation on deposit quality. All photographs focus on the wirebond pad itself. At this location, the bonding pads are closest together and extraneous or inadequate plating carries the greatest impact. Figure 9a and b shows a wirebond pad before and after plating, respectively, with bath 1. Before plating, the grain structure of the immersion gold around the outer perimeter of the wirebond pad consists of elongated crystal domains. This is likely the result of enhanced nonlinear diffusion of reacting molecules at the edge. Further, the grain structures are more spherical. After the electroless gold plate, the grain size remains similar though the edges are less well defined.

Figure 10a is the result of plating with the low hydroxide bath (bath 5). In this bath, no plating was recorded; instead an intergranular corrosion was observed. Energy-dispersive spectrophotometry (EDS) spectra of this surface reveals a higher proportion of Ni to Au, indicating that a portion of the immersion gold was stripped away due to insufficient hydroxide concentration. Figure 10b-e illustrates the effect of various additives on the resulting morphology of the electroless gold deposit. Both SA (bath 7, Fig. 10b) and chloride ion (bath 8, Fig. 10c) appear to increase the mound size by

favoring vertical and equilateral growth equally. The bath containing 1,5-NDSA (Fig. 10d, bath 9) yields the thickest deposit and enhances lateral growth, likely through strong chemisorption at the gold surface. The wirebond sample plated in the presence of HQSA similarly exhibits smooth crystal domains. These results qualitatively demonstrate that adsorption of additive molecules to the substrate surface during plating leads to smoother finishes, and some molecules, such as 1,5-NDSA, are more effective at yielding smooth electroless plated surfaces than others.

Conclusion

The utility of the EQCM as a screening tool for determination of electroless gold plating efficiency was presented. The adsorption of the reactive intermediate, or the true reducing agent, in a DMABbased bath is detectable by EQCM and is correlated to plating rates obtained on industrial wirebond monitor samples. It is found that an increase in mass is observed at the gold surface at the potential for gold oxide reduction on the cathodic scan. This mass increase is attributed to the adsorption of the reactive intermediate to the gold surface upon reactivation of DMAB oxidation, and is a direct measure of the extent of interaction of the reducing agent with the gold surface. Baths exhibiting a greater extent of interaction (surface adsorption), as is the case in the presence of organic additives, generally yield higher plating rates. It can be envisioned that this method could be extended to any electroless bath where chemisorption of the reducing agent to the substrate surface plays a major role in the deposition process.

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