Electrochemical Measurement Of the Activity of Printable Catalysts Used for Electroless Metallization

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Direct metallization of dielectric substrates for flex-circuits or fabrics for EM shielding by electroless method requires the use of "once-through" or printable catalysts. The mixed-potential time data have been used to evaluate the activity of printable catalysts. The activity of the catalysts was related to the minimum time required to reach a steady-state mixed-potential. Catalysts activated under varying conditions were compared. Results obtained show that the approach gives a reliable method of measuring catalyst activity. With very good control of bath conditions, the method is useful for comparative purposes and useful also as a tool for improving catalyst performance and elucidating the role of catalyst active ingredients.

Fully additive circuitry or one-step metallization where the desired circuit pattern is directly plated onto a dielectric layer^{1,2} is of interest because the method allows finer lines and spaces, and offers better heat and chemical resistance because no adhesive layer is used. The technique allows thin metallization where required, thereby saving catalysts and reducing waste. Unlike the conventional method of catalysis in which the entire substrate is catalyzed and photomasks used to activate a selected portion of the substrate, the "onestep" metallization technique requires the selected portion of the substrate to be directly printed with a catalyst and activated before plating. The one-step method is also suitable for unconnected (multiple) patterns and metallization of fabrics used for EM shielding. Electroless plating is the preferred method for depositing the metal on the dielectric substrate because there is no underlying conductive path to allow electrolytic plating. Interest in the field of fully-additive pattern plating has therefore resulted in extensive research and development directed towards improving the method by which the catalyst pattern is printed and activated on the dielectric (catalyzation step), bath stability (plating step) and mechanical properties of the deposits^{3,4}. In the catalyzation step, a solution of palladium salt is mixed with an appropriate carrier polymer to form a printing ink. A printer or printing press is then used to print the circuit patterns on the dielectric. For the EM shielding fabric, a catalyst of very low viscosity is used for catalyzation. The fabric substrate is first passed through a processing tank of the catalyst solution guided by rollers. As the fabric exits the tank, it is passed through a roller or squeegee to reduce the amount of catalyst on the substrate. After drying, quite unlike the conventional PdCl₂/SnCl₄ activation step for electroless plating, the printed or catalyzed substrates are activated thermally or photochemically.

Unfortunately, the catalyst activation step has been found to be a rate limiting (determining) step. For thermal activation, the temperature of activation and time of activation are important factors that determine the activity level of the



Fig. 1—Potential-time curve for uncatalyzed nickel in electroless copper bath.



Fig. 2—Mixed-potential changes in electroless copper bath for nickel catalyzed and activated ($150 \, ^{\circ}C$) for different times. The arrow shows the initial inflection point for the 60-min activation time.

catalyst.⁵ Because of the requirements of good printability, adhesion, and stability (non-blistering) in the electroless bath, the catalyst ink may contain several additives that affect its activity. There is, therefore, a need to have a method by which the activity of a given catalyst formulation can quickly be estimated or determined and compared to other formulations. Such a method can be used as a tool in improving catalyst performance and elucidating the role of various active ingredients in the catalyst. There are many methods by which activity of catalysts can be determined and compared. These approaches include:

- (a) Determination of the resistance of a plated sample for a given plating period.
- (b) Comparison of cyclic voltammetric peak currents of the metal ion reducing agent used in the electroless bath.
- (c) Comparison of the "induction period" (time) required for attainment of the mixed-potential of the initialization of electroless plating.



Fig. 3—AFM images of nickel sample catalyzed and activated at 150 °C for 45 min: (A) 3-D; (B) flattened.

Each method above has some associated merits and demerits. For instance, the time required to get a conductive surface, as in (a), can be very subjective. Defining this time is made more difficult if the metallic deposit is highly conductive. The cyclic voltammetric approach is attractive because the partial anodic reaction of the reductant⁶⁻¹⁰ and hydrogen sorption in Pd¹¹ has been related to the catalytic behavior of the substrate. The cyclic voltammetric method depends on the solution pH because the anodic oxidation of the reductant increases with increasing solution pH. Despite this, many reports have related the catalytic activity of a substrate to the peak current or the potential (at a referenced current density)⁷ of the bath reductant. The current or potential is often obtained from a solution that lacks most of the chemical components found in a typical electroless bath. Because the solutions used for the measurement of catalyst activity through the cyclic voltammetric technique do not often contain all the active ingredients found in a typical electroless bath, it is probable that the measured current (or potential), and hence, the predicted catalyst activity differ from the true catalyst activity.

Similarly, the induction period method depends on the composition of the electroless solution. Accordingly, a fair and appropriate comparison of catalysts requires the use of experimental baths that are identical to a typical electroless bath. Horkans⁹ pointed out that the use of mixed-potential measurement for catalyst activity was challenging because of high variability often observed. This is true if the source of the variability is ignored in the experimental set-up. As is shown later, this variability can be minimized if the bath conditions are kept constant. Both the induction time and the cyclic voltammetry methods also require the use of conductive substrates. It is expected that the higher the activity of a catalyst, the shorter the time (induction time) required to nucleate the surface of a substrate with the metal deposit. In addition to this, a catalyst of higher activity exhibits a higher oxidation current for the reductant than a catalyst of lower activity.

The literature on one-step additive pattern plating is very scanty. For the substrate catalyzation, Sausa *et al.*³ investigated laser decomposition of platinum metallo-organic films for electroless copper plating. The substrate was coated by spun-on platinum metallo-organic film, and by focusing an ion laser on the film, it was activated and used for electroless plating. Kondo *et al.*¹¹ photoreduced palladium organic-complexes on an alumina substrate and employed electroless plating on the surface. It was also pointed out that thermal or photochemical means could be used to activate the catalyst; however, the activity of the catalyst was not investigated.

Tokas *et al.*¹² described a catalyzation process similar to the one used in this study. Polyimide was used as the carrier polymer in their work, but they did not investigate the activity of the catalyst.

As a catalytic process, electroless metallization needs palladium seeding for its initiation. The palladium seeding reduces the time required for the substrate surface to acquire a potential favorable for the initial metal deposits to be formed. This time that elapses before the plating potential is reached is often referred to as the induction period. The induction period on a non-catalytic substrate appears to decrease on the application of a catalyst. Even for catalyzed substrates, application of accelerators tends to decrease the induction period. This is attributed to the role of accelerators in changing the surface of the palladium seeding used for catalyzation. The nature and distribution of the palladium seeds determine the catalytic activity of the surface.^{5,8} It is expected that the activity of surfaces catalyzed with the same catalyst and metallized in a bath of similar characteristics can be compared through determination of their induction periods.

Theory

Consider an electrochemical reaction j written as

$$\sum_{i} s_{ij} M_i^{z_i} \to n_j e^- \tag{1}$$

where s_{ij} is the stoichiometric coefficient of species *i* in reaction j, n_j is the number of electrons transferred in reaction j and z_i is the charge number of molecular species M_i . For a redox reaction, the partial current densities are represented by the Butler-Volmer equations as follows:

$$i_{j}^{a} = i_{aj}^{a} \left[\exp\left(\frac{\alpha_{aj}F}{RT}\eta_{j}\right) \right]$$
(2)

for the anodic reaction and

$$i_{j}^{e} = -i_{oj}^{e} \left[\exp \left(-\frac{\alpha_{oj}F}{RT} \eta_{j} \right) \right]$$
(3)

for the cathodic reaction. Here, i_{oj} is the exchange current density, α_{aj} (anodic) and α_{cj} (cathodic) are the transfer coefficients. The surface overpotential η_i is given by



Fig. 4—Variation of steady-state mixed potential time (catalyst activity) with catalyst activation temperature.

$$\eta_j = E_d - \phi_o - U_{j,o} \tag{4}$$

where E_d and ϕ_o are the electrode potential and solution potential adjacent to the electrode surface, respectively. $U_{j,o}$ is the theoretical open-circuit potential for reaction j at the surface concentrations of species j. For a general reference electrode (represented with subscript RE) placed near the substrate, the theoretical open-circuit potential is given by¹³

$$U_{j,\sigma} = U_j^{\theta} - \frac{RT}{n_j F} \left[\sum_i s_{ij} \ln\left(\frac{c_{i,\sigma}}{\rho_o}\right) \right] - \left[U_{BS}^{\theta} - \frac{RT}{n_{RE}F} \sum_i s_{i,SE} \ln\left(\frac{c_{i,SE}}{\rho_o}\right) \right] (5)$$

 $U_{j,o}$ is the standard electrode potential for reaction j, $c_{i,o}$ is the local surface concentration of species c, ρ_o is pure solvent density and subscripts RE and ref are used for the reference electrode.

The anodic and cathodic exchange current densities are expressed, respectively, as

$$i_{oj}^{a} = i_{oj,ref}^{a} \prod_{i} \left(\frac{c_{i,o}}{c_{i,ref}} \right)^{\gamma_{ij}} \left[Cat - a \right]^{\omega} \quad (6)$$

$$i_{oj}^{c} = i_{oj,ref}^{c} \prod_{i} \left(\frac{c_{i,o}}{c_{i,ref}} \right)^{\gamma_{ij}} \left[Cat - c \right]^{\zeta}$$
(7)

where γ_{ij} is the exponent in the concentration dependence of the exchange current density.

 $[Cat-a]^{\omega}$ and $[Cat-c]^{\xi}$ are used to refer to a combination of both surface conditions and species concentrations that do not appear in the overall reaction but attenuate the rate of the reactions. The exponents appearing on the concentration terms in Eqs. (6) and (7) are given by

$$p_{ij} = \gamma_{ij} + \frac{\alpha_{ij} s_{ij}}{n_j}$$
(8)

$$q_{ij} = \gamma_{ij} - \frac{\alpha_{ij} s_{ij}}{n_j} \tag{9}$$



Fig. 5—Grain size growth with activation temperature (activation time, 45 min).

In Eqs. (8) and (9), $p_{ij} = s_{ij}$ and $q_{ij} = 0$, if $s_{ij} > 0$, else if $s_{ij} < 0$, $q_{ij} = -s_{ij}$ and $p_{ij} = 0$.

Using the approach of White *et al.*,¹³ we can recast equations (2) and (3) as

$$i_{j}^{a} = i_{gj,eqf}^{a} \left[Cat - a \right]^{e} \prod_{i} \left(\frac{c_{i,e}}{c_{i,eqf}} \right)^{e_{e}} \exp \left[\frac{\alpha_{ef}F}{RT} \left(E_{d} - \phi_{RE} - U_{j,eqf}^{a} \right) \right] (10)$$
$$i_{j}^{e} = -i_{ej,eqf}^{e} \left[Cat - c \right]^{e} \prod_{i} \left(\frac{c_{i,e}}{c_{i,eqf}} \right)^{e_{q}} \exp \left[-\frac{\alpha_{ef}F}{RT} \left(E_{d} - \phi_{RE} - U_{j,eqf}^{e} \right) \right] (11)$$

Comparison of Eqs. (10) and (11) with Eqs. (2) and (3) shows that the exchange current density (assumed to be a good approximate measure of catalytic activity of the electrode) is dependent on the catalytic terms. Further, at equilibrium, the mixed-potential theory postulates that

$$\dot{\boldsymbol{i}}_{j}^{a} = \left| \dot{\boldsymbol{i}}_{j}^{c} \right| \tag{12}$$

The potential associated with this equilibrium condition is the mixed-potential and corresponds to

$$E_{mp} = E_d - \phi_{RE}$$

Applying the above and solving for E_{mp} from Eqs. (10) and (11) obtain

$$E_{ap} = -\frac{1}{\beta} \ln \left(\frac{i_{gl,af}^{*}}{i_{gl,af}^{*}} \right) - \frac{1}{\beta} \sum_{i} \left(p_{g} - q_{g} \right) \ln \left(\frac{c_{i,\rho}}{c_{i,af}} \right) - \frac{\lambda}{\beta} - \frac{\omega}{\beta\zeta} \ln(Cat)$$
(13)

where β and λ are defined as

$$\beta = \frac{F}{RT} (\alpha_a + \alpha_c) \tag{14}$$

$$\lambda = \frac{F}{RT} \left(\alpha_a U^a_{j,ref} + \alpha_c U^e_{j,ref} \right)$$
(15)

$$(Cat) = \frac{[Cat - a]}{[Cat - c]}$$
(16)

^a Advanced Performance Materials, St. Louis, MO.



Fig. 6-Mixed-potential time data for Cu foils in electroless copper bath.



Fig. 7—Effects of catalyst coating thickness (catalyst C2) on the mixed potential variation in the electroless copper bath.

In Eq. (13), $E_{mp}(t)$, $c_{i,o}(t)$ and Cat (t) are dependent on time. At the initiation of deposition, however, the change in $c_{i,0}(t)$ with time is very small compared to the changes in Cat (t) brought about by the activity of new surfaces and catalytic species. Thus, during this initial period, the dependence of $E_{mp}(t)$ on time is purely a result of the catalytic activity of the substrate on which deposition is occurring. After the substrate has become totally covered with the fresh metal film deposit, a near constant E_{mp} (t), independent of changing surface film, will be obtained. This is true because the catalytic activity of the deposit is thought to remain nearly constant when the active species concentration, $c_{i,0}$ changes at a slow rate. Consequently, by following the changes in E_{mp} during the initiation period, the activity of a catalyzed surface can be correlated with the time period required to acquire a constant mixed potential. It is postulated that the more active the catalyst, the shorter the initiation time.

In this investigation, the induction period method was used to study the activity of catalyst inks formulated for the additive pattern plating. The goal was to explore the feasibility of using the induction period technique to provide a quantitative measure of the activity of catalysts for comparative purposes.

Experimental Procedure

Solution A was prepared by dissolving 72.3 grams of polyvinyl butyral in 400 mL of methanol with vigorous stirring. In a separate container, 0.77 g palladium acetate was dissolved in 2.3 g ammonium hydroxide and stirred until the acetate was completely dissolved to form solution B. Solution B was slowly added to A with stirring to form the catalyst ink. The catalyst ink was used to coat (using draw-blade rollers) on ultrasonically cleaned nickel samples. Similarly, ink without palladium ions was also prepared and used to catalyze some samples. Following catalyzation, the samples were dried and activated at various times and temperatures. The catalyzed and uncatalyzed nickel samples were used to measure the "induction period" of the electroless copper bath.

In another set of experiments, three commercial catalyst inks,^a C1, C2 and C3 (Advanced Performance Materials, MO, USA) based on three different carrier polymers (polyvinyl chloride, polyamic acid and polyurethane, respectively) were used to catalyze copper substrates. Following the activation step (the activation conditions are proprietary information), the mixed potential for the initialization of electroless copper on the samples was followed as a function of time. A commercial electroless copper bath was used in all runs.

Results & Discussion

The effect of temperature and time of activation on catalyst activity was investigated by following the mixed-potential (E_m) palladium-ink catalyzed nickel and copper samples. The mixed-potential-time curve for an uncatalyzed and unactivated nickel sample in an electroless copper bath is shown in Fig. 1. Copper deposition cannot be initiated on nickel in the absence of a catalyst because nickel does not catalyze HCHO oxidation. Accordingly, the potential-time curve for the nickel sample is seen to increase in the noble direction relative to the starting potential. Thus, there is no identifiable mixed-potential in the figure. In the absence of palladium in the ink, a result similar to Fig. 1 is expected if a copper substrate sample is immersed in an electroless nickel bath.

Figure 2 shows the results obtained when catalyzed nickel samples were activated at 150 °C. As activation time increases, the mixed potential for the sample becomes more negative. In addition to the more negative increase in potential at higher activation times, an inflection in the potentialtime curve is observed. This inflection occurs before a steady-state potential (mixed potential) value is reached. The length of time it takes for the inflection to appear seems to vary with the time of catalyst activation. For instance, in Fig. 2, the observed times for the inflections are 59, 53 and 44 sec for the samples activated for 15, 45 and 60 min, respectively. The interesting observation, however, is the variation in the length of time it takes for the mixed-potential of each catalyzed sample to reach a steady-state (level out) value. It appears to be a function of the activation time. A close examination of the data obtained at 15-min activation time shows that the steady state mixed-potential attained was very tenuous, quite unlike the data obtained at the longer activation time periods. In addition to the weak (not well-defined) steady-state mixed potential region for the 15-min activated sample (in comparison to the 45-min or the 60-min sample), a physical examination of the sample showed the absence of nucleated copper at the end of the immersion time in the bath. This is in contrast to the samples activated at longer time periods. Figure 3 shows 3-D and flattened AFM images of a 150 °C catalyzed and activated sample (45 min activation time). The distribution of palladium particles observed is not uniform. This may play a significant role in the subsequent activity of the catalyst layer.

Figure 4 summarizes the results obtained for two activation times studied. The figure shows that as the activation time increases (for a given activation temperature), the time required for the catalyzed sample to reach a steady-state mixed potential in the bath decreases. The minimum time required to attain a steady mixed potential is here regarded as

Table 1 Mixed-potential Data for Copper Samples

Sample	First I Tim	nflecti ie, sec	on Point E, V	Mixed Potentia Time, sec	al (\mathbf{E}_{m}) \mathbf{E}, \mathbf{V} 0.670
Date copper		04	-0.020	204	-0.070
C1-A: catalyze not activated Catalyst C1	ed, -			112	-0.734
C1-B: catalyze activated with Catalyst C1	ed, 1	.7	-0.977	82	-1.091
C2: catalyzed, activated with Catalyst C2	8	31	-0.909	312	-1.116
C3: catalyzed, activated with Catalyst C3	1	2	-1.026	137	-1.225

Table 2
Mixed-potential Data
For Freshly Deposited Electroless Copper

Sample	First Inflecti	on Point	Mixed Potential (E _m)				
	Time, sec	E, V	Time, sec	E, V			
No catalyst	4.2	-0.916	15.2	-1.191			
Catalyzed &	12.7	-0.808	57.3	-1.142			
activated							
Catalyzed.	15.5	-1.036	29.7	-1.141			
activated &							
accelerated							
Sample accelerated in mixture of hydroxime, NaOH & HCHO; catalyst: C1.							

the time required for complete copper nucleation of the nickel sample surface. The ease of nucleation is assumed to be proportional to the catalyst activity, thus the minimum time required for a steady-state mixed potential is used as a measure of the catalyst activity. Consequently, Fig. 4 indicates that the catalyst activity increases with increase in activation temperature for any given activation time. It also shows that (within the narrow temperature and time ranges of this study) the activity of the catalyst increases with catalyst activation time at a given temperature. The results obtained for activation conditions of 15 min and 150 °C show that minimum energy conditions (*i.e.*, the product of activation time and input thermal energy. Heat input per unit time (power) is proportional to the activation.

In a previous study,⁵ the activated catalyst grain size diameter was observed to increase with activation temperature. Figure 5 shows the relationship between the activation temperature and grain size diameter for the 45-min-activated samples shown in Fig. 4. The grain size diameter increases with temperature as expected, inasmuch as a higher activation temperature favors a greater growth rate for the agglomerating palladium particles that result from the reduction of the palladium ion.

The characteristics of the mixed-potential time results for the commercial catalysts were similar to those observed in the polyvinyl-butyral-based catalyst. Figure 6 shows a comparison of results obtained with catalyst C1 for bare (uncatalyzed) copper, unactivated (catalyzed) and activated (catalyzed) copper samples. Two time periods were observed for some of the catalyzed samples: (i) a small "inflection" in the potential-time curve and (ii) a second period in which the gradient of the potential-time curve is nearly zero. This second period is again assumed to reflect an equilibrium condition when the initialization of electroless copper has been completed. The results obtained for the commercial catalysts with copper substrates are summarized in Table 1. Based on the mixed-potential time in the fourth column of the table, the method does indeed provide the necessary activity information. It can be seen that a "clean" copper sheet is less active than when the same material is catalyzed and activated. The results also indicate that catalyst C1 is the most active of the three. This is in agreement with the observations of the catalyst supplier.

The effect of a catalyst on a freshly deposited copper surface was evaluated--electroless copper deposited on mylar was compared to similar samples that were catalyzed with catalyst C1. The results obtained are summarized in Table 2. The result shows that the fresh copper surface that is not catalyzed is more active than the catalyzed copper. This observation does not contradict an earlier observation in which another copper sample (cleaned commercial copper) was observed to be less active than the catalyzed copper. Whereas results of Table 2 were based on freshly deposited electroless copper, those of Table 1 used commercial electrolytic copper. The results in Table 2 thus show the importance of a fresh copper surface in the autocatalytic process.

The effect of catalyst coating thickness on the time required to attain equilibrium mixed potential was studied. Figure 7 shows a comparison between coating thickness of 4.5 µm and 2.5 µm with catalyst C2. A slight difference in the measured time for steady-state mixed potential was observed. Whereas it took 372 sec for the 2.5-µm-thick catalyst to reach a steady-state mixed potential, 388 sec were required for the thicker catalyst. Possibly, the differences observed are related to the differences in the transport of the active species (mass transfer resistance) to the catalyst particles. Thinner films will probably offer lower resistance than thicker films, thus reducing the time required to achieve a steady state mixed-potential. Figure 7 suggests that the initial inflection point observed on the mixed-potential time curves might include effects resulting from catalyst thickness. In addition to the effects of catalyst thickness, the observed differences may include the effects of such other factors as the species concentrations and bath condition, as pointed out earlier in the derivation of the mixed-potential time equation [Eq. (13)]. The significance of the result is that a fair comparison of catalyst activities must be based on the same conditions, including catalyst thickness and bath conditions. Thus, the utility of the method could be appreciated if a number is assigned to the induction time of, say, Cu in an electroless bath of known characteristics. Using such base data, more quantitative information could be obtained regarding the effect of activation temperature, active catalyst components etc. on the activity of a given catalyst.

Conclusions

The mixed-potential time data for a printable catalyst has been used to evaluate electroless catalyst activity. A method

by which catalytic activity is measured is seen to be beneficial to the electroless plating industry in the quantitative comparison of catalyst formulations. For a catalyst ink manufacturer, the technique described can be used to enhance quality control and productivity. Further, it can aid the understanding of the role of the active ingredients used in the catalyst formulation. The method can also be used to define more precisely the optimal activation conditions (temperature and time) for a given catalyst.

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