Characterization of PdSn catalysts for electroless metal deposition

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A set of electrochemical techniques has been developed to measure the component concentrations and the catalytic activity of the PdSn seeder solutions used to activate insulating substrates for the electroless deposition of Cu. The concentration of Sn(II) was calculated from the limiting current for Sn(II) oxidation, that of Sn(IV) from the difference between the Sn metal-deposition limiting current and the Sn(II) limiting current. The palladium concentration was determined by a stripping analysis after Pd deposition from an oxidized seeder solution. The catalytic activity of the PdSn catalyst was estimated by measuring its activity for the electro-oxidation of formaldehyde (the reducing agent used in the electroless Cu bath) or by the cyclic voltammetric response of a seeded electrode in an inert electrolyte. The cyclic voltammetric technique and transmission electron microscopy examination were used to evaluate various accelerating solutions used to increase the activity of the seeder.

Introduction

Numerous applications, including many in the electronics industry, require a reliable and economical means of depositing a metal film on an insulating substrate. This goal can often be accomplished by using electroless deposition. In the fabrication of the multilayer printed circuit boards used for the IBM 3081 processor, for example, a glass-reinforced epoxy dielectric board is metallized with a Cu conductor [1]. The Cu must be deposited as lines on the surface, as interlevel connections, and in plated through holes which receive connectors. Vacuum deposition of the Cu is not feasible because of the scale and topography of the board. Electrodeposition cannot be employed, because the board is an insulator. Thus, electroless deposition is the favored technique for deposition of at least the initial layer of the Cu; the Cu thickness can then be built up by electrodeposition.

The confusingly named technique of electroless deposition accomplishes the reduction of a metal ion in solution to a metallic atom on the surface by using a reducing agent in the solution. Electrodeposition achieves the same end with an external electromotive force (EMF). The use of the reducing agent in solution to provide the EMF eliminates the necessity of making electrical contact to the unit to be plated. The Cu^{2+} must be complexed in order to keep it in solution at the desired pH. Formaldehyde (HCHO) is the most commonly used reducing agent. Electroless Cu deposition is described in [2–7]. The prior deposition of a suitable catalyst on the surface ensures that the reaction between the complexed metal ion and the reducing agent proceeds only where a deposit is desired.

The technology of catalyzing electroless deposition has evolved over the years. Current practice generally employs as catalyst a Pd-containing colloid, referred to here as PdSn. The PdSn catalysts are commercially available materials, and their preparation and use are described in the patent literature (e.g., [8–12]). The catalysts are prepared by mixing

$PdCl_2$ with a large excess of $SnCl_2$ in HCl solution. The surface to be activated, i.e., catalyzed, is immersed in the catalyst, depositing metallic Pd (which is the catalytic material) as well as Sn(II). A solution known as an accelerator is usually used to remove the tin species from the surface before initiation of the plating reaction.

When PdSn catalysts first came into general use, there was a controversy about whether they are true solutions or colloids. Thus, many of the early studies of these materials sought to characterize them. Ultracentrifugation of the catalysts causes the precipitation of a solid component [13, 14], showing that they are colloidal suspensions rather than solutions. The colloidal nature of the PdSn activating solutions was also established by ^{119}Sn Mössbauer spectroscopy [13, 15]; the state of the Pd is inferred from the tin spectrum. The observations are consistent with the following model: The catalyst is a colloid having a metallic core of the order of 1 nm in diameter, consisting mainly of Pd but also containing a small amount of Sn; the colloid is stabilized by the adsorption of Sn(II) and its associated counter-ions on the metallic core.

Rutherford backscattering (RBS) [16] and Mössbauer spectroscopy [17] were subsequently used to examine the individual steps in the activation of graphite with PdSn. The PdSn colloid and an excess of tin are adsorbed on the graphite surface in the activation step. A large excess of $Sn(OH)_4$ remains after rinsing with water but is removed by the accelerator. The metallic core is not removed by the rinse or by the accelerator. The coverage of $Sn(OH)_4$ is further decreased in the early stages of electroless Cu plating.

Electron diffraction and electron microscopy are useful for examining the PdSn colloid on surfaces. The published studies employing these techniques disagree markedly, however. Matijevic et al. [14] support the colloid model of PdSn catalysts, whereas others [18, 19] dispute the existence of a colloid. Cohen and West [17] claim that the studies that dispute the colloid model [18, 19] can be alternatively interpreted to agree with a colloidal catalyst. Additionally, Matijevic et al. [14] point out that the absence of light scattering from a solution does not prove the absence of a colloid. Osaka et al. [20] and Horkans et al. [21] have used electron microscopy to investigate the effect of different accelerators on the PdSn catalyst layer. Horkans et al. [21] prepared thin epoxy samples for direct transmission electron microscopy on substrates chemically similar to epoxy boards. Grunwald et al. [22] used Auger electron spectroscopy to characterize the steps of activation and acceleration.

It is also useful to have a method for the direct evaluation of the catalytic activity of the PdSn colloids. Electrochemical techniques show promise for this purpose. One simple method of measuring PdSn activity is the monitoring of the mixed potential of an activated surface as electroless plating is initiated [23, 24]. The initiation time is shorter for more active catalysts. Voltammetry of colloid-covered surfaces has also been used to evaluate the catalysts [23–25]. Osaka et al. [23] adsorbed the colloid on a Au electrode, then stripped it from the surface with a positive-going potential sweep. The charges under the stripping peaks could be taken as a measure of the surface coverages of Pd and tin. The amount of Pd on the surface is not a direct measure of catalytic activity, however, since activity can be affected by a number of factors. Horkans [24, 25] showed an example of two colloids resulting in similar Pd coverages but having very different catalytic activities; in the cyclic voltammetry of activated Cu electrodes in dilute $HClO_4$, the current peak due to hydrogen desorption from Pd was used as a measure of the accessibility of the Pd catalytic centers. Tam [26] used *in situ* voltammetry to determine the Sn(II) and Sn(IV) content of PdSn activators and used an *ex situ* stripping technique to determine Pd.

The present paper describes a number of electrochemical methods for characterizing the catalytic activity of PdSn deposits as well as for determining the concentrations of the tin and palladium species in the catalytic solution. The techniques were used to evaluate new and aged PdSn suspensions and to evaluate the effects of different accelerating solutions.

Experimental methods

The use of cyclic voltammetry to evaluate activated surfaces was described by Horkans; the experimental details are given in [24]. In this technique, evaporated Cu films were subjected to the activation and acceleration steps and rinsed. The cyclic voltammetry of this activated surface was then measured in dilute $HClO_4$.

For the other experiments, the electrochemical cell was a conventional three-compartment glass cell. The counter-electrode was a platinum flag, and the reference electrode was saturated calomel (SCE). All potentials are reported vs. SCE. The cell was fitted with a port allowing the solution to be purged with argon. Glassy carbon (GC) is well suited to the characterization of the adsorbed PdSn catalyst because there are no interfering reactions occurring at the GC surface over the potential range of interest. Glassy carbon disk electrodes of area 0.196 cm^2 (Pine Instruments) were polished with successively finer grades of alumina, finishing with 0.05 μm alumina. They were then cycled between −0.6 V and 0.8 V in 1.0 mol/dm^3 HCl until a reproducible, time-independent background current was obtained, usually about 10 minutes. Some of the measurements employed Au electrodes, which were polished in the same way as the GC. The GC electrodes were modified after the electrochemical pretreatment by immersing them in the PdSn catalyst solution for one minute. This step was usually followed by immersion ("acceleration") in 1.0 mol/dm^3 HCl for one minute. The electrodes were then transferred directly to the electrochemical cell.

The PdSn catalyst was obtained from Sel-Rex. All chemicals were reagent grade except the ultrapure H_2SO_4 (Ultrex, Baker). The formaldehyde solutions were prepared daily, immediately before use, from 37% solution (Sargent Welch). The solutions were prepared with H_2O purified by a Millipore water reagent system. All solutions were de-aerated with argon to avoid air oxidation of Sn(II).

Electrochemical measurements were made with a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat, a PAR Model 175 programmer, and a PAR Model 179 digital coulometer. The data were recorded on a Yokagawa 3033 X–Y recorder.

Direct transmission electron microscopy (TEM) through transparent epoxy samples was described in [21]. The substrate was a Si wafer having a number of Si_3N_4-covered windows. The epoxy was spun on the wafer and cured. Except for areas where the epoxy had balled up to form thick, opaque regions, the combined thickness of the Si_3N_4 membrane and the epoxy was low enough to allow electron transmission. These epoxy-covered samples were accelerated, activated, and briefly plated with Cu, then examined using TEM.

Compositional analysis of the PdSn colloid system

In order to maintain the colloidal integrity of the PdSn catalyst system and hence its optimal catalytic activity, it is thought necessary that the composition of the catalyst solution not vary significantly over the period of its use. It is thus highly desirable to have simple, reliable methods for analyzing the PdSn catalyst. The rotating-disk and rotating-ring-disk electrodes are powerful systems for kinetic and mechanistic studies and analytical determinations, since they enable one to vary the rate of mass transport over a very wide range. For potentials where the surface concentration of the electro-active species is zero, the equation relating the diffusion-limiting current density i_L and the electrode rotation rate ω is the Levich equation [27],

$$i_L = 0.62nFD^{2/3}\nu^{-1/6}c_0\omega^{1/2}. \quad (1)$$

In this equation, n is the number of electrons per mole of reactant, F is Faraday's constant, D is the diffusion coefficient of the reacting species, ν is the kinematic viscosity of the solution, and c_0 is the bulk concentration of the reacting species. For an electrode reaction purely under mass transport control, a plot of i_L vs. $\omega^{1/2}$ should be linear and pass through the origin. Further, a plot of i_L vs. c_0 for a fixed rotation rate should be linear, with an intercept of zero. The latter type of plot can be used as a calibration to determine the concentrations of electro-active species. The following sections describe methods that have been developed to determine the tin and palladium concentrations in the PdSn colloidal solution and to estimate the palladium coverage on an activated surface.

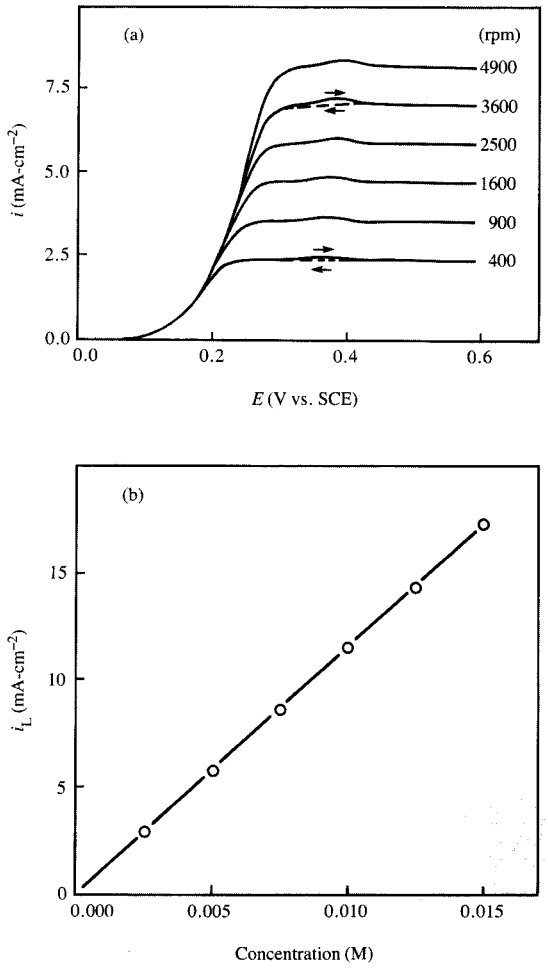

Figure 1

(a) Polarization curves for Sn(II) oxidation at a Au RDE in diluted seeder solution (solution diluted × 100 with 1.0 mol/dm^3 HCl) at 23°C. Potential sweep rate = 10 mV/s. (b) Diffusion-limiting current as a function of Sn(II) concentration. Rotation rate = 900 rpm. Potential sweep rate = 10 mV/s.

Determination of stannous concentration

The concentration of free Sn(II) in PdSn colloidal solutions was determined by measuring i_L for Sn(II) oxidation to Sn(IV) in a chloride solution containing a known amount of the PdSn seeder solution. Either gold or glassy carbon could be used as the rotating disk electrode (RDE).

Typical polarization curves (current density vs. electrode potential) for Sn(II) oxidation at a Au RDE at various rotation rates are shown in **Figure 1(a)**. The solution was 1.0 mol/dm^3 HCl containing 1 vol % of the PdSn seeder solution. The curves exhibit fairly well defined limiting-

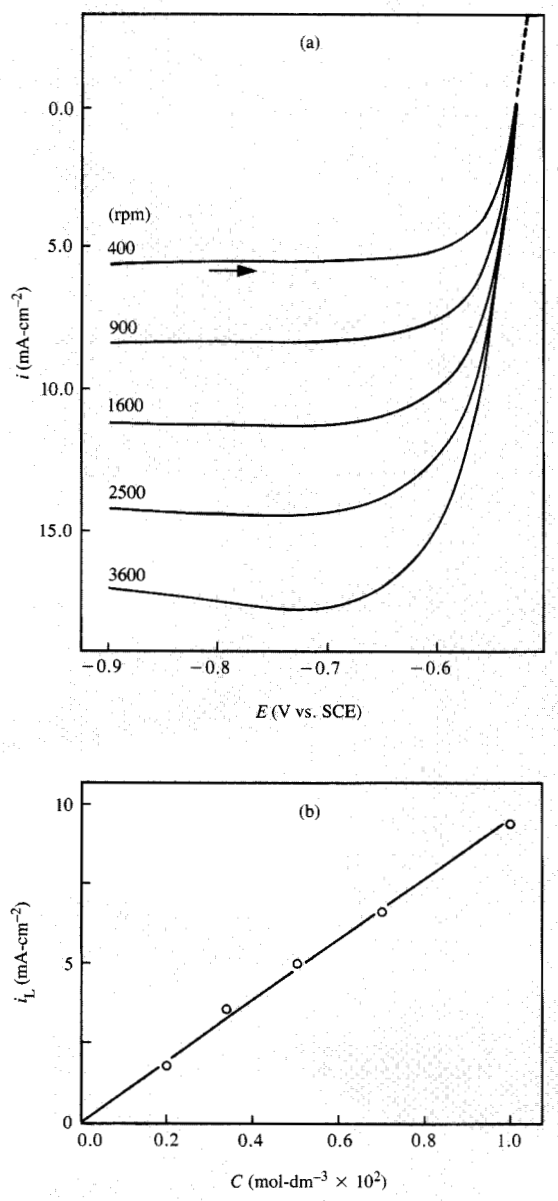

Figure 2

(a) Polarization curves for Sn electrodeposition at a glassy carbon RDE in 1.0 mol/dm^3 HCl + 1.5 mol/dm^3 NaCl + 10^{-2} mol/dm^3 $SnCl_4$ at 23°C. Potential sweep rate = 20 mV/s. (b) Diffusion-limiting current as a function of Sn(IV) concentration. Rotation rate = 900 rpm. Potential sweep rate = 20 mV/s.

current regions. The limiting currents obey the Levich equation [Equation (1)] for a convective diffusion-limited process. The currents at the foot of the curves were somewhat irreproducible and depended on the direction of the potential sweep and on the electrode pretreatment. Small amounts of PdSn particles, ionic palladium, or Sn(IV) in solution have not been found to cause significant variations in the steady-state limiting currents for the Sn(II) oxidation reaction. The electrodissolution of PdSn particles adsorbed on the GC electrode causes the minor bumps in the limiting current at approximately 0.35 V when the potential is swept in the positive direction. Polarization curves similar to those in Figure 1(a) were obtained at Au for Sn(II) oxidation in electrolyte that contained $SnCl_2$ but no PdSn particles. A calibration plot of diffusion-limiting current vs. Sn(II) concentration in a chloride-containing solution is shown in **Figure 1(b)** for a Au RDE.

Gold was found to be the most suitable electrode for Sn(II) oxidation to Sn(IV). Platinum had initial activity comparable to Au for Sn(II) oxidation but lost activity rapidly during potential cycling and required frequent polishing. Glassy carbon also exhibited activity for Sn(II) oxidation to Sn(IV) in PdSn seeder solution, but the kinetics of Sn(II) electro-oxidation were found to be slow. Diffusion-limiting currents were observed at relatively high potentials at GC, above approximately 1.0 V in 1.0 mol/dm^3 HCl. The polarization curves obtained for GC were very reproducible, however, and gave a linear calibration plot of Sn(II) oxidation diffusion-limiting current vs. Sn(II) concentration.

Determination of stannic concentration

The concentration of Sn(IV) can in principle be determined by measuring either the diffusion-limiting current for Sn(IV) reduction to Sn(II) or the limiting current for Sn electrodeposition from both Sn(II) and Sn(IV) species. The use of the Sn(IV) + $2e^- \rightarrow$ Sn(II) reaction to determine Sn(IV) is not promising because of the lack of a well-defined diffusion-limiting current for this reaction, and because of the difficulty of separating the current for the Sn(IV)-to-Sn(II) reduction reaction from the current due to Sn electrodeposition. The best results were obtained with electrolytes containing relatively high concentrations of either NaBr or NaCl, e.g., 4–8 mol/dm^3 (see [28]), but the use of such concentrated solutions is not usually convenient. Irreproducible results were obtained in chloride solutions of concentration 3 mol/dm^3 or less, regardless of the electrode material. The Sn electrodeposition reaction was therefore the better choice as the method for determining the concentration of Sn(IV). Since the Sn(II) concentration is known from the stannous determination described above, the Sn(IV) concentration is easily calculable from the difference between the total tin concentration and the stannous concentration.

Gold and GC were found to be the most suitable electrode materials for Sn deposition. A supporting solution of 1 mol/dm^3 HCl + 1.5 mol/dm^3 NaCl gave well-defined diffusion-limiting currents at the RDE. Polarization curves for Sn deposition at a GC RDE in 10^{-2} mol/dm^3 $SnCl_4$ are shown in **Figure 2(a)** for various electrode rotation rates.

The curves were recorded by stepping the potential of the electrode to −900 mV (SCE), holding for 5 s, and then sweeping the potential in the positive direction at 20 mV/s. For rotation rates less than approximately 2500 rpm, fairly well defined limiting currents were obtained. Similar electrodeposition curves were obtained for Sn(II) solutions and mixed Sn(II)/Sn(IV) solutions. At potentials more negative than −0.7 V, plots of i^{-1} vs. $\omega^{-1/2}$ were fairly linear with essentially zero intercepts for $\omega \leq 2500$ rpm, indicating that the deposition of Sn was mass-transport controlled for these conditions. Plots of i_L vs. Sn(IV) concentration were linear, with zero intercepts for a number of different electrolytes. The best reproducibility was obtained for the mixed NaCl/HCl electrolyte; a calibration plot of i_L vs. Sn(IV) concentration is shown for this electrolyte in **Figure 2(b)**.

The electrodeposition current of Figure 2(a) gives the sum of the concentrations of Sn(IV) and Sn(II) species. If the absolute value of the previously determined current due to oxidation of Sn(II) to Sn(IV) is subtracted from the electrodeposition current, the remainder is due to the reduction of Sn(IV) to Sn(0). This current can be used to determine the Sn(IV) concentration from the calibration curve. The method assumes equal diffusion coefficients for Sn(II) and Sn(IV). This assumption was found to be valid within experimental error. Glassy carbon generally gave better-defined diffusion-limiting currents than Au.

Determination of palladium concentration

The palladium content of the PdSn colloidal solutions was determined by an anodic stripping analysis. The metallic Pd in the seeder solution was first converted to Pd^{2+} by the addition of approximately 0.2 ml 30% H_2O_2/50 ml. (This procedure simultaneously converted all of the tin to the 4+ oxidation state.) The Pd was then deposited onto a rotating disk electrode, and the charge necessary to strip this layer was measured. Palladium deposition-stripping curves recorded at a GC RDE are shown in **Figure 3(a)**. The electrolyte was 1.0 mol/dm^3 HCl + 0.01 mol/dm^3 $PdCl_2$. The amount of Pd deposited in the deposition step is dependent on the lower potential limit and on the electrode rotation rate. Palladium deposition initiates at a potential slightly more positive than 0 V in the negative-going potential sweep, and continues to occur in the potential range of −0.20 to 0.25 V in the positive-going sweep. The main peak observed at approximately 0.5 V is due to Pd stripping. Stripping data were obtained after first conditioning the GC RDE at 800 mV for 60 s, then stepping the potential to −175 mV for 30 s, and finally sweeping the potential in the positive direction at 50 mV/s. The charge associated with the Pd stripping peak at approximately 0.5 V was used in the construction of the calibration plot in **Figure 3(b)**; the plot is linear over the concentration range shown but does not intercept the origin. Similar calibration plots were constructed for palladium solutions containing Sn(IV). Working seeder solutions were analyzed using both standard analytical procedures and the deposition-stripping method.

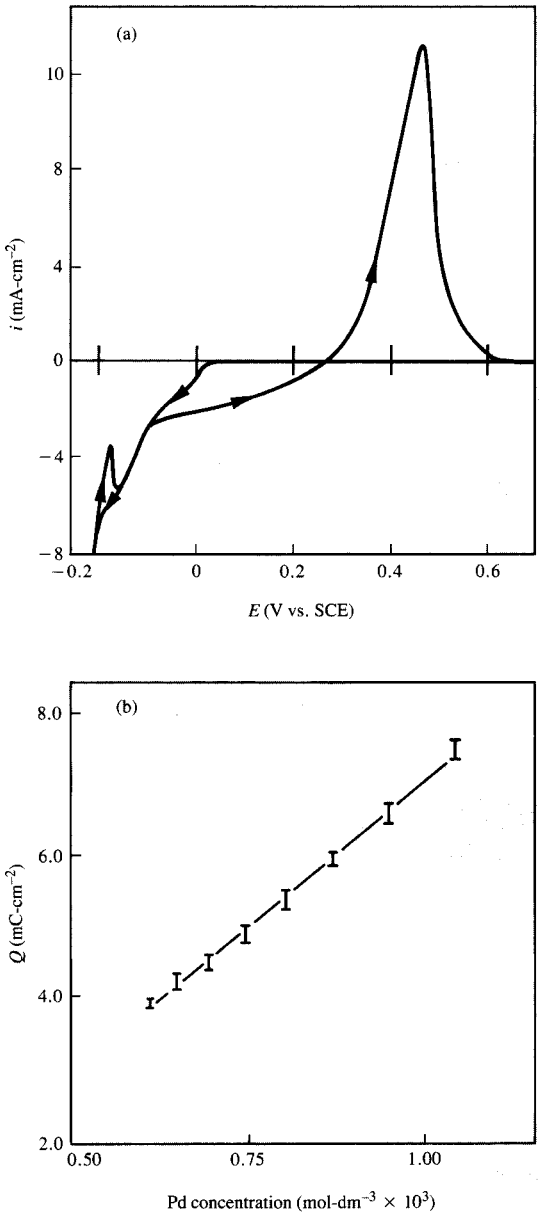

Figure 3

(a) Voltammogram of a GC electrode in 10^{-2} mol/dm^3 $PdCl_2$ + 1.0 mol/dm^3 HCl at 22°C. Potential sweep rate = 20 mV/s; rotation rate = 3600 rpm. (b) Palladium stripping charge as a function of Pd^{2+} concentration in 1.0 mol/dm^3 HCl + 1.5 mol/dm^3 NaCl. Text gives details of Pd deposition process. Rotation rate = 1600 rpm. Potential sweep rate = 50 mV/s.

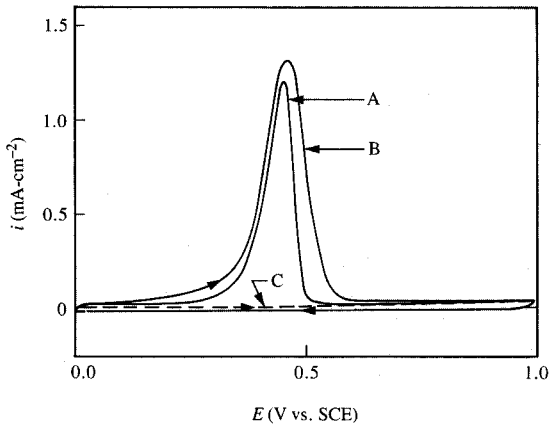

Figure 4

Palladium stripping curves for a PdSn-seeded GC electrode in 1.0 mol/dm^3 HCl. Curve A: Acceleration in 1.0 mol/dm^3 HCl. Curve B: No acceleration. Curve C: Second and subsequent cycles. Sweep rate = 100 mV/s.

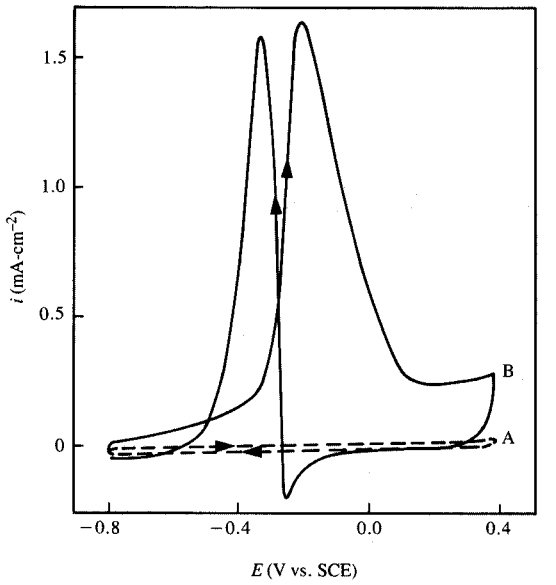

Figure 5

Voltammogram of PdSn-seeded GC electrode in 1.0 mol/dm^3 $NaSO_4$ + 0.01 mol/dm^3 NaOH + 2×10^{-3} mol/dm^3 HCHO. Curve A: Clean GC surface. Curve B: PdSn-seeded GC surface (accelerated in 1.0 mol/dm^3 HCl).

The two methods showed good agreement. Thus, the deposition-stripping technique is potentially useful for determining the Pd concentrations of PdSn seeder solutions that have been appropriately diluted.

Estimation of Pd surface coverage

Stripping techniques can also be used to estimate surface coverages on GC electrodes activated by PdSn seeders, as shown in **Figure 4**. The 1 mol/dm^3 HCl could be used as the electrolyte for the stripping analysis, even though it is the same solution used as the accelerator, because the electrode is potentiostatted at 0.0 V immediately after the electrolyte is introduced. The potential of the seeded electrode was swept in a positive direction from its initial potential of 0.0 V. On the first scan, a single large stripping peak was observed at 0.45 V. Subsequent scans showed only the double-layer charging current attributable to a clean GC surface. The charge densities, corresponding to the integrated area of the peak, were typically 1.8×10^{-3} C/cm^2 and 3.7×10^{-3} C/cm^2 for accelerated and unaccelerated PdSn-coated surfaces, respectively. Curve B, for the unaccelerated electrode, exhibited a shoulder near 0.25 V, which is apparently due to the stripping of stannous tin from the stabilizing layer of the unaccelerated sample. This behavior is consistent with that observed by Osaka et al. [23] on a seeded Au electrode. One cannot, however, rule out the possibility that the shoulder is partly a broadening effect due to inhomogeneity of the seeded electrode in the presence of tin. Assuming that the dissolution is a two-electron process, the measured charges correspond to Pd surface coverages of 5.6×10^{15} atoms/cm^2 and 11.6×10^{15} atoms/cm^2 for accelerated and unaccelerated samples, respectively. These coverages agree with those determined by Meek using Rutherford backscattering [16]. Since Meek observed little variation in coverages between graphite and glass–epoxy substrates, the electrochemical behavior of seeded electrodes such as GC should give insight into the behavior of the PdSn catalyst on insulator surfaces like epoxy.

Methods of evaluating catalytic activity

The quantitative techniques discussed above are important in evaluating seeders and maintaining them in day-to-day operation. These techniques are not direct measures of the catalytic activity of the seeders, however. The methods discussed below have been found to give reliable estimates of the catalytic activity of PdSn colloids.

Cyclic voltammetry of PdSn-coated GC in formaldehyde

The activity of the seeder can be assessed by determining its ability to catalyze the oxidation of HCHO, a reductant commonly used in electroless Cu baths. The oxidation of HCHO is the rate-limiting reaction in the electroless deposition of Cu [6]. In **Figure 5**, the bare unseeded GC surface (Curve A) shows no activity for HCHO oxidation.

The seeded GC surface (Curve B) exhibits peaks for HCHO oxidation at approximately −0.18 V in the positive-going sweep and at approximately −0.42 V in the negative-going sweep. Repetitive potential cycling resulted in a decrease in the peak currents. This apparent decrease in catalytic activity with potential cycling may be partly related to electrodissolution of the PdSn particles during potential cycling and to changes in the surface composition of the particles. A qualitative comparison of catalytic activities for HCHO oxidation (and hence catalytic activities for initiating electroless plating) can be obtained from curves like the one in Figure 5 from either the peak currents or the charges under the peaks. (The shape of these HCHO-oxidation curves and the dependence of the peak position on sweep direction are complex functions of the surface state of the electrode and its history. It is not necessary to consider these matters in order to evaluate the seeder activity. A more complete discussion of the oxidation of formaldehyde and other organic compounds can be found, for example, in [29, 30].)

In order to assess the electro-activity of seeded GC electrodes for electro-oxidation of HCHO as a measure of seed catalytic activity, HCHO-oxidation results were compared with mixed-potential (E_m) measurements of the initiation of electroless Cu deposition. The time required for E_m to reach the potential of the electroless Cu bath is the so-called "take time." Although the activity of PdSn catalysts can be determined by E_m measurements, this technique has the disadvantage that any variability of the electroless Cu bath will introduce variability unrelated to the PdSn seeder. The "take-time" measurements monitored the E_m of seeded Ta rods in an electroless Cu bath. (Tantalum is a readily available and inexpensive substrate for these measurements. It forms an inactive, insulating oxide film that is stable in the electroless Cu solution.) The electroless Cu bath contained EDTA as complexant and HCHO as reducing agent and operated at 72°C. The Ta rod was seeded and accelerated by the same procedure used for the GC electrode. Since there was some variability in the measurements of mixed potentials, the reported times are the averages of several trials. The potential of unseeded Ta was approximately 0.63 V and was invariant with time. When the Ta surface was seeded, a Cu-plating potential of −0.8 V was obtained, and visible deposits of Cu were observed.

The measurements of E_m and HCHO electro-oxidation were compared for active and inactive seeders. A PdSn solution stored under Ar was used as the active seeder and control sample. A sample of the same solution was slowly deactivated over time by stirring under a stream of O_2. The detrimental effects of O_2 on the PdSn solution have been pointed out by Cohen and West [13]. The loss of seed-bath catalytic activity can be understood as follows. The Sn(II), probably present as chloride complexes on the colloid surface, serves to limit the initial size of the colloid and to impart a charge sufficient to prevent flocculation. The O_2 oxidizes the Sn(II) and destroys the stabilizing Sn(II) layer. The consequence of prolonged exposure to oxygen is flocculation of material and poor catalytic activity. During the course of several days, both the degraded and the control aliquots were tested for their electrochemical activity for HCHO oxidation, and "take times" were measured for Ta seeded with these solutions. The Sn(II) concentrations were measured as described above.

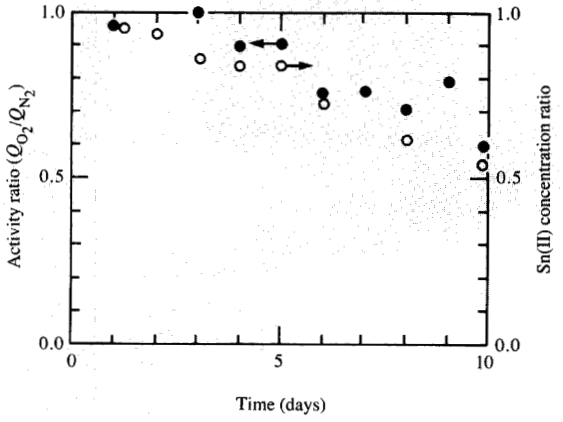

Figure 6

Variation of PdSn catalytic activity, expressed as Q(oxygen)/Q(control) for HCHO oxidation activity, and of Sn(II) concentration, expressed as $i_{L(O_2)}/i_{L(N_2)}$, with time of exposure of seed solution to oxygen gas.

Table 1 Electroless Cu deposition "take time" for oxygen-treated PdSn seeder solution.

Oxygen-treatment time (days)	*Take time* (s)
0	25
4	44
7	49
9	68

The parameter selected to represent activity from the cyclic voltammetric measurements was the charge associated with the HCHO electro-oxidation peak at approximately −0.4 V in the negative-going potential scan. This quantity had a value of $1.44 \pm 0.21 \times 10^{-4}$C/cm^2 for the control sample. **Figure 6** gives the ratio of the HCHO-oxidation charges for the oxygen-treated sample and for the control, shown as Q_{O_2}/Q_{N_2}. Also shown in Figure 6 is the ratio of Sn(II) concentrations in the oxygen-treated and control samples, determined from the ratio $i_{L(O_2)}/i_{L(N_2)}$. "Take-time" values as a function of oxygen-treatment time are shown in **Table 1** for the degraded samples.

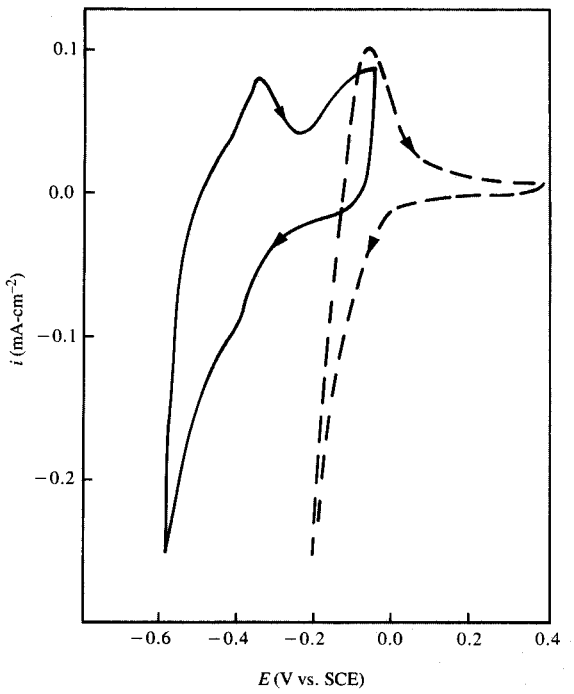

Figure 7

Cyclic voltammetry in 0.01 mol/dm^3 $HClO_4$ of pure Pd foil (dashed curve) and a Cu film electrode activated with a PdSn colloid (solid curve). Sweep speed = 20 mV/s.

It is evident from Figure 6 that measurement of HCHO-oxidation catalytic activity gives a reasonably good assessment of PdSn catalyst activity, since the decrease in Q_{O_2} is also accompanied by an increase in "take time." Further, the correlation between $i_{L(O_2)}/i_{L(N_2)}$ and Sn(II) concentration is quite good. The latter result suggests the need to control the concentration of Sn(II) for optimum performance of the seed bath. After an additional six days, $i_{L(O_2)}/i_{L(N_2)}$ for solution-phase Sn(II) fell to 0.43, while the charge ratio Q_{O_2}/Q_{N_2} for HCHO oxidation fell to 0.15. Ultimately the Sn(II) concentration reached zero, and no catalytic activity was observed for HCHO oxidation. When this occurred, the colloid solution was found to be completely flocculated. The Ta rods catalyzed in these flocculated solutions did not reach the Cu plating potential when placed in an electroless Cu bath.

Evaluation of activity using cyclic voltammetry

Cyclic voltammetry of activated electrodes in inert electrolytes can also be used to give information about the PdSn colloid. The colloid was adsorbed on a Cu-film electrode and the cyclic voltammetry was recorded in dilute $HClO_4$, an electrolyte not containing strongly adsorbing anions. Use of this electrolyte thus allows the measurements of currents characteristic of the electrode surface without the interference of currents due to adsorption from solution. A typical cyclic voltammogram of an activated Cu-film electrode in 0.01 mol/dm^3 $HClO_4$ is shown in **Figure 7**. The cyclic voltammetry of a Pd foil electrode is also shown for comparison.

The potential region shown for Pd is that in which hydrogen is sorbed and desorbed. As the potential is swept toward the negative potential limit, hydrogen is adsorbed on and absorbed in Pd below approximately −0.1 V. After the reverse of the sweep, this hydrogen is desorbed, giving a peak at approximately −0.1 V. The process is essentially complete at approximately 0.1 V. The exact shape of the curve depends on the sweep conditions, the pH of the solution, and the crystallographic structure of the Pd.

The curve for activated Cu electrodes was described in detail in [24, 25]. Three features should be pointed out. First, the Sn(II)/Sn(IV) couple results in a peak at approximately −0.1 V in the positive-going sweep [Sn(II) → Sn(IV) + $2e^-$] and as a barely visible shoulder at approximately −0.4 V on the major peak in the negative-going sweep [Sn(IV) + $2e^-$ → Sn(II)]. In these curves, the Sn(II)/Sn(IV) peaks are not sufficiently separated from the other features to allow integration of the charge due to tin, but comparable peaks can be measured on Cu treated with $SnCl_2$ colloids not containing Pd. For $SnCl_2$-covered Cu, the charge under these peaks gives a relative measure of the tin coverage but is not quantitative, perhaps because not all of the adsorbed tin species are in electrical contact with the electrode. The relative amounts of stannic and stannous tin originally on the surface cannot be distinguished by this technique, because the potential sweep changes the oxidation state of the tin. The second important feature of the curve in Figure 7 is the lack of a Cu-dissolution current in this potential range, which shows that the Cu surface is covered by tin species. Third, the presence of Pd is indicated by hydrogen-sorption currents, which occur at more negative potentials than on pure Pd (i.e., this process requires more energy on PdSn colloids than on pure Pd). The large reduction current in the negative-going sweep is due to adsorption and absorption of hydrogen in Pd. The adsorbed and absorbed hydrogen is reoxidized in the peak at approximately −0.35 V in the anodic sweep. The height of this peak can be used as a measure of the availability of the Pd for catalysis of the electroless deposition reaction.

References [24, 25] discuss in more detail the information that can be obtained with this method. It has been used to monitor a working PdSn catalyst and has shown good correlation with functional tests of activity ("take-time" measurements).

The technique has been used to compare the action of various accelerator solutions. Examples are shown in Figures

8–10. The shape of the curve is significantly changed when the Cu electrode is accelerated after activation. A 1 mol/dm^3 HCl accelerator gives the behavior shown in **Figure 8**. Acceleration (the removal of tin species from the surface) decreases the magnitude of the tin peaks. There is also an indication of lower tin coverage: A copper-oxidation current is observed at the positive limit of the positive-going sweep. The peak due to the desorption of hydrogen from Pd is shifted to less negative potentials, i.e., toward the potential of hydrogen desorption from bulk Pd. The hydrogen-desorption peak appears at approximately −0.3 V in Figure 8 compared to approximately −0.35 V in Figure 7. The behavior in the negative-going sweep is greatly changed by HCl acceleration: A peak is observed, rather than the monotonically increasing current of Figure 7. The size of this peak may represent the total of adsorbed and absorbed hydrogen, which is limited by the amount of Pd available. Although H_2 evolution is thermodynamically possible at these potentials, it does not occur. The reason that HCl acceleration so dramatically changes the shape of the negative sweep is not understood. Other accelerators were found to affect the cyclic voltammetry similarly to HCl. Examples of such compounds are NH_4BF_4 and NH_4HF_2.

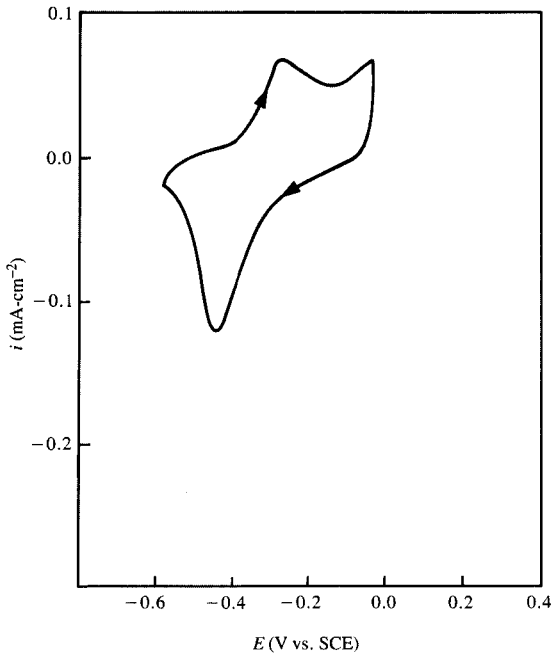

Figure 8

Cyclic voltammetry in 0.01 mol/dm^3 $HClO_4$ of a Cu film electrode activated with a PdSn colloid and accelerated for 1 min in 1 mol/dm^3 HCl. Sweep speed = 20 mV/s.

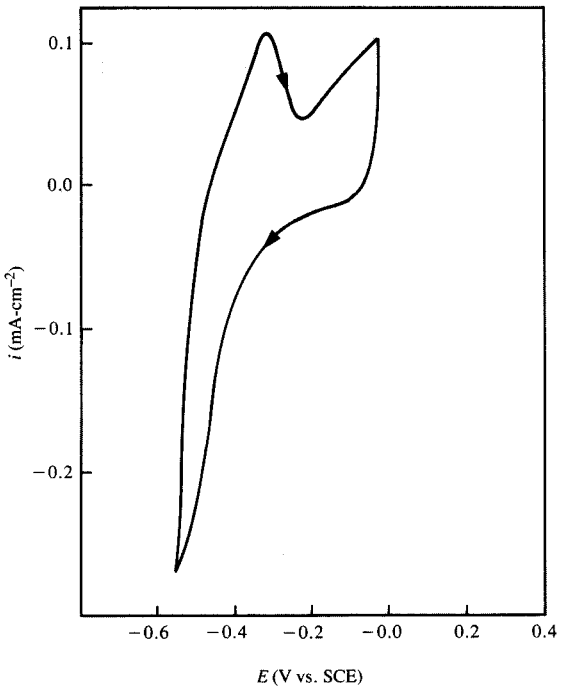

Figure 9

Cyclic voltammetry in 0.01 mol/dm^3 $HClO_4$ of a Cu film electrode activated with a PdSn colloid and accelerated for 1 min in 0.13 mol/dm^3 EDTA at pH 12. Sweep speed = 20 mV/s.

Cyclic voltammetry after acceleration with EDTA is shown in **Figure 9**. The main effect of EDTA is to increase the magnitude of the hydrogen-desorption peak. The EDTA apparently makes the Pd nuclei more accessible but does not greatly change their environment. The hypothesis of greater Pd accessibility after EDTA acceleration is in agreement with the excellent performance of EDTA accelerators in functional tests. The EDTA is a highly versatile accelerator because it can be used over a wide pH range. Similar results are obtained when the EDTA solution has an acidic pH of 4.5.

Sodium hydroxide has an effect qualitatively very different from that of any other accelerator examined. After NaOH acceleration, none of the major peaks of the colloid is observed, as shown in **Figure 10**. No Sn(II)/Sn(IV) peaks appear. There is a hydrogen adsorption/absorption current in the negative-going sweep, but no clear desorption peak in the positive-going sweep. It is known [31], however, that the shape of the hydrogen-desorption peak on Pd is strongly dependent on the grain size. There is evidence (see below) that NaOH acceleration results in the catalyst's being distributed on the surface mainly as small individual

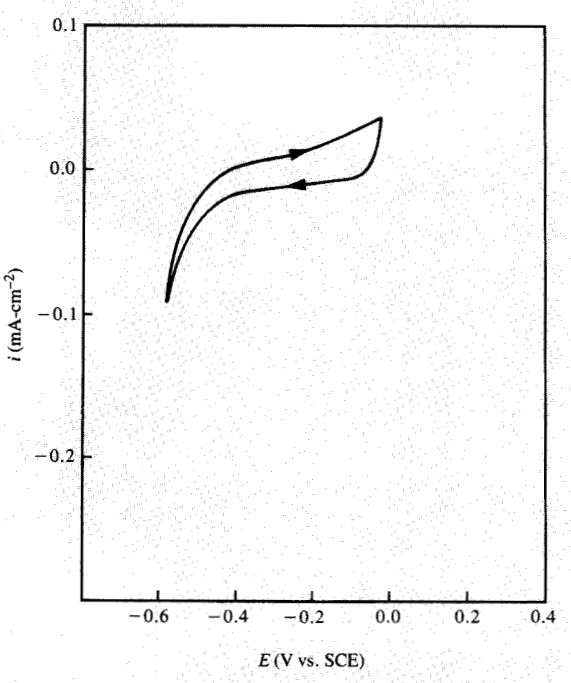

Figure 10

Cyclic voltammetry in 0.01 mol/dm^3 $HClO_4$ of a Cu film electrode activated with a PdSn colloid and accelerated for 1 min in 1 mol/dm^3 NaOH. Sweep speed = 20 mV/s.

particles, in contrast to the distribution of both individual particles and agglomerates resulting after acceleration with HCl or EDTA. The desorption of hydrogen from these small particles apparently occurs over a very broad energy range.

Ammonia can also be used as an accelerator. Like NaOH, NH_3 decreases all of the major peaks in the cyclic voltammetry, but the effect is much smaller. The Sn(II)/Sn(IV) couple can still be clearly discerned, although it is lower than for an unaccelerated sample, indicating removal of tin. The hydrogen sorption and desorption currents are lower than for unaccelerated samples, but not as low as for samples accelerated with NaOH. Since 1 mol/dm^3 NH_3 is only slightly lower in pH than 1 mol/dm^3 NaOH, it is likely that there are chemical differences in the workings of these two accelerators.

Transmission electron microscopy of activated epoxy

Further information about PdSn activation and about the action of accelerators can be gained through transmission electron microscopy (TEM). The examination of activated and accelerated epoxy surfaces and the preparation of electron-transmitting epoxy samples by means of TEM were described in detail in [21]. The catalyst particles were decorated (i.e., their visibility was enhanced) by briefly plating electroless Cu on the activated epoxy surfaces. (Electroless Cu was plated for 120 s for the samples shown here. The effects of plating time are shown in [21].) Although TEM is capable of very high resolution, a low magnification was used in order to show the distribution of particles on the surface.

The results are shown in **Figure 11**. As described in [21], the preparation of the thin epoxy films left some thick regions that are opaque in TEM. These appear as large, dark areas in this figure, but the Cu particles can be observed in the light, transmitting areas between these regions. The appearance of the unaccelerated epoxy surface is shown at the top left. Even after 120 s of plating, the Cu deposit is not yet continuous on the surface. The Cu exists on the surface in widely dispersed clumps with smaller, more uniformly distributed Cu nuclei between them. (At this magnification, the small nuclei are barely resolved dots and even the clumps are small features.) The larger clumps are probably Cu plated on agglomerated PdSn particles and the smaller nuclei Cu plated on individual PdSn particles.

The earlier stages of electroless Cu deposition proceed faster when the activation step is followed by an accelerator. The effect of acceleration is also shown in Figure 11. Energy-dispersive X-ray analysis of these samples confirmed that deposition initiates faster after acceleration. The Cu on the accelerated samples, as on the unaccelerated sample, is distributed as larger clumps and small nuclei. Such a distribution was also observed by Osaka et al. [20]. After acceleration, the Cu tends to be more distributed as clumps; the extent of the increased clumping depends on the accelerator used. It appears that acceleration can lead to agglomeration of PdSn particles. The Cu deposition initiates faster after NaOH acceleration than after acceleration using HCl or EDTA. More of the Cu exists as small particles when NaOH is used than when the other two accelerators are used. After HCl acceleration, most of the Cu is in large clumps. The EDTA gives a Cu-particle distribution intermediate to those obtained using HCl and NaOH.

Conclusions

It has been demonstrated that a variety of electrochemical methods can be used for quantitative electroanalytical determination of PdSn seeder solution components and electrochemical assessments of catalytic activity. Use of these techniques to monitor the behavior of seeder solutions over time ensures constant chemical composition and consistent catalytic activity. Rotating-disk methods can be used to determine the concentrations of Sn(II), Sn(IV), and Pd in the PdSn solutions. Although such methods are extremely convenient, they have not previously been mentioned in the literature in connection with this type of application. These quantitative analyses could easily be automated. Quantitative analyses are insufficient for describing the catalytic activity of a seeder, however. Characterization of

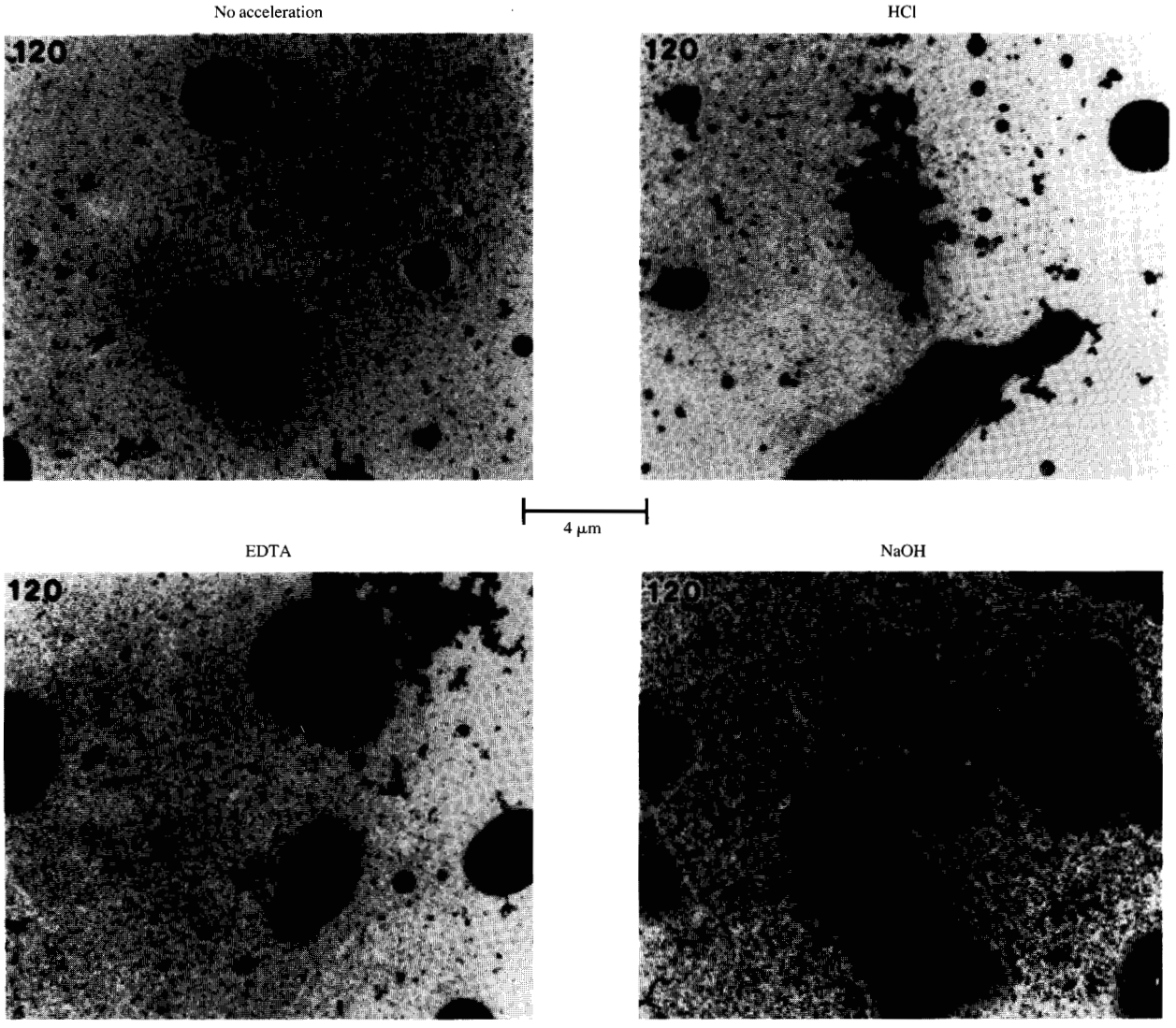

Figure 11

Direct TEMs through epoxy films activated with PdSn colloid, accelerated, and then plated for 120 s with electroless Cu. The accelerators used were the same as those used for the samples of Figures 7–10: none, HCl, EDTA, and NaOH. The TEM work was through the courtesy of J. Kim.

seeded Cu surfaces in inert electrolytes was shown to give information that supplements the quantitative information [24]. This technique was particularly useful in evaluating accelerating solutions and identifying promising new accelerators. The electrochemical assessment of PdSn seed activity based on the oxidation of HCHO has also been described. Such testing is amenable to on-line monitoring of the catalytic activity of PdSn seeder solutions. Further, use of modified glassy carbon electrodes demonstrates promise for future studies to elucidate some of the fundamental processes occurring at the interface between the seed surface and the plating solution.

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