Initiation of electroless Cu plating on nonmetallic surfaces

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Electroless plating of a metal on a dielectric substrate requires the prior deposition of a catalyst such as a Pd-Sn colloid consisting of a metallic Pd core surrounded by a stabilizing layer of Sn ions. The activation step (deposition of the colloid) is usually followed by an acceleration step (removal of excess ionic tin). Adhesion of the deposit to the substrate is improved by mechanical and chemical pretreatment steps. An electrochemical method has been developed for assessing the catalytic activity of Pd-Sn colloids. Hydrogen sorption in the Pd in the colloid can be correlated with catalytic activity, since Pd accessible for the H-sorption reaction is also accessible as the catalyst for the electroless deposition reaction. These conclusions have been confirmed by surface analytical techniques and by functional tests. The efficacy of various accelerating solutions has also been assessed.

Introduction

The fabrication of a printed circuit board (PCB) entails the formation of a pattern of conducting lines on a nonconducting substrate, e.g., Cu lines on an epoxy board. A variety of feasible techniques is available for the fabrication process; among these, the electrochemical technique of electroless deposition has proven to be extremely useful. A critical step of electroless deposition is the initiation of the process on the dielectric substrate. We have sought a better understanding of the initiation of electroless deposition and have developed analytic tools to monitor the process.

In electroless deposition, the driving force for reducing an ion in solution to a metal on the surface is provided by introducing a reducing agent homogeneously in the solution. The solution is inherently unstable: The reaction between the metal ion and the reducing agent is thermodynamically possible, both homogeneously in the solution and heterogeneously at the surface. The successful practice of the technique depends on the introduction of a suitable catalyst on the surface, making the heterogeneous reaction much more likely than the homogeneous reaction.

A number of metals and alloys can be deposited electrolessly, but we confine ourselves to the discussion of electroless copper. During electroless Cu deposition, two electrochemical reactions are proceeding simultaneously on the surface—the reduction of copper ions to Cu and the oxidation of the reducing agent, formaldehyde, to the formate ion. The potential of the plating surface is the mixed potential [1, 2], i.e., the potential at which the rates of the oxidation (anodic) and reduction (cathodic) processes are equal. It is known [3] that the copper-reduction reaction is reversible, its rate being determined by the copper ion concentration at the surface, and that the formaldehyde-oxidation reaction is under kinetic control. Catalyzing the overall process is thus basically a matter of choosing a good catalyst for the formaldehyde reaction.

The catalysis of formaldehyde oxidation is an important topic outside the scope of this paper. A detailed discussion of the catalysis is given by Bindra et al. [4]. The first step of the reaction is the dissociative adsorption of formaldehyde (HCHO) into an adsorbed carbon-containing fragment and adsorbed hydrogen. Thus Pt, which adsorbs hydrogen, can be used to catalyze electroless Cu deposition, but Au, which does not adsorb hydrogen, cannot. The formaldehyde reaction is impeded by the formation of surface oxides, and thus non-noble metals are not good catalysts. Strongly bound intermediates of the reaction can also poison the process.

The catalyst most commonly used to activate surfaces for electroless Cu deposition is Pd. It is quite noble, can both adsorb and absorb hydrogen, and is economically feasible to use. Oxide-free copper is also a good catalyst, and thus the plating process continues once it is initiated.

The Pd catalyst must be placed on the surface of the dielectric to be plated, e.g., glass-reinforced epoxy board. An older method of doing this involved immersing the board in a solution of $SnCl_2$ [5] to deposit tin(II) ions on the surface. The board was next immersed in a solution of $PdCl_2$. The adsorbed Sn(II) reduced the Pd(II) to Pd metal on the surface. There are several drawbacks to activating a surface in this way. One of the most serious is that the $PdCl_2$ solution attacks any Cu metal that may be present, forming a thick and poorly adherent Pd deposit.

A more modern procedure is the immersion of the board in a suspension of a Pd-Sn colloid. In this material, the Pd is already in the metallic state. The structure of the colloid is known [6] to be a metallic Pd core, containing also a small amount of Sn metal, surrounded by a stabilizing layer of Sn(II) and associated anions. The overall charge on the colloid particle is negative. Once the colloid is on the surface, the ionic tin no longer plays a role; it can in fact bury the Pd core and detract from the activity of the catalyst. Excess tin is usually removed by a solution called an accelerator [7], which is a solvent for ionic tin. Common accelerators are solutions of HCl, NaOH, NH_4BF_4, and NH_4HF_2.

The application of electrochemical methods to the characterization of Pd-Sn colloids has been described in a previous publication [8], which also gives greater detail about earlier studies of Pd-Sn colloids and the controversy concerning the nature of these materials. Moessbauer spectroscopy [7] and electrochemical stripping techniques [9] have been used to characterize the colloids and to examine the effects of each of the activation and acceleration steps. The activity of a catalyst is most frequently evaluated by using functional tests; however, these can be misleading because of the difficulty of separating the activity of the catalyst from the "activity" of the electroless Cu solution used in the functional test. We have developed electrochemical techniques [8] for measuring the accessibility of Pd catalysts on activated surfaces. The electrochemical results are corroborated by other surface analytical methods.

In practice, measures must be taken to ensure good adhesion of the metal deposit to the dielectric substrate. Treatments of the substrate prior to the activation step can improve adhesion by a) mechanically creating a network to which the catalyst and the subsequent deposit can be physically anchored and b) chemically modifying the surface to provide sites that can react with the colloid particle. Initial work [10, 11] emphasized mechanical interactions; it employed various means to physically roughen the surface (i.e., sanding, sandblasting, etc.) and various aggressive etchants to produce a network of fine pits. It was subsequently shown [12] that chemical etching solutions promote adhesion by a chemical mechanism as well as by mechanical interlocking. Chemical treatments also convert a hydrophobic to a hydrophilic surface. The reactions of the catalyst with the treated organic surface are discussed elsewhere [13–16]. Plasma techniques can also be used to alter the surface characteristics of the polymeric substrate; they have the advantage of not producing wastes that need to be processed.

Proper monitoring and control is an important part of the activation process. Examples are given here of the information that electrochemical methods can yield about the activation and acceleration steps prior to electroless deposition. The ways in which this information differs from information obtained using other surface analytic techniques are discussed.

Analytic techniques

The electrochemical technique used in these studies is cyclic voltammetry. A triangular potential program is applied to a working electrode, and the resulting current flow is measured as a function of the electrode potential. This procedure requires three electrodes. The potential between the working electrode and a reference electrode is controlled by a potentiostat. In order to maintain the imposed potential, a current flows between the working electrode and an auxiliary electrode. The reference electrode used here is the mercurous sulfate electrode (MSE), which has a potential of 0.68 V vs the normal hydrogen electrode. The auxiliary electrode was a high-surface-area Pt screen.

The use of cyclic voltammetry to study Pd-Sn colloids has been described elsewhere [8]. The working electrode was a thin evaporated Cu film that had been immersed in the colloidal suspension for five minutes and rinsed. It was then mounted in a glass and Kel-F cell. The Pd-Sn colloid was prepared by diluting a concentrate, similar to that described by Zeblisky [17], with a NaCl solution. The electrolyte for the cyclic voltammetry was 0.01 M $HClO_4$, chosen because it does not strongly attack either the Cu electrode or the Pd-Sn colloid and because it does not contain strongly adsorbing ions. The solution was de-aerated with bubbling N_2.

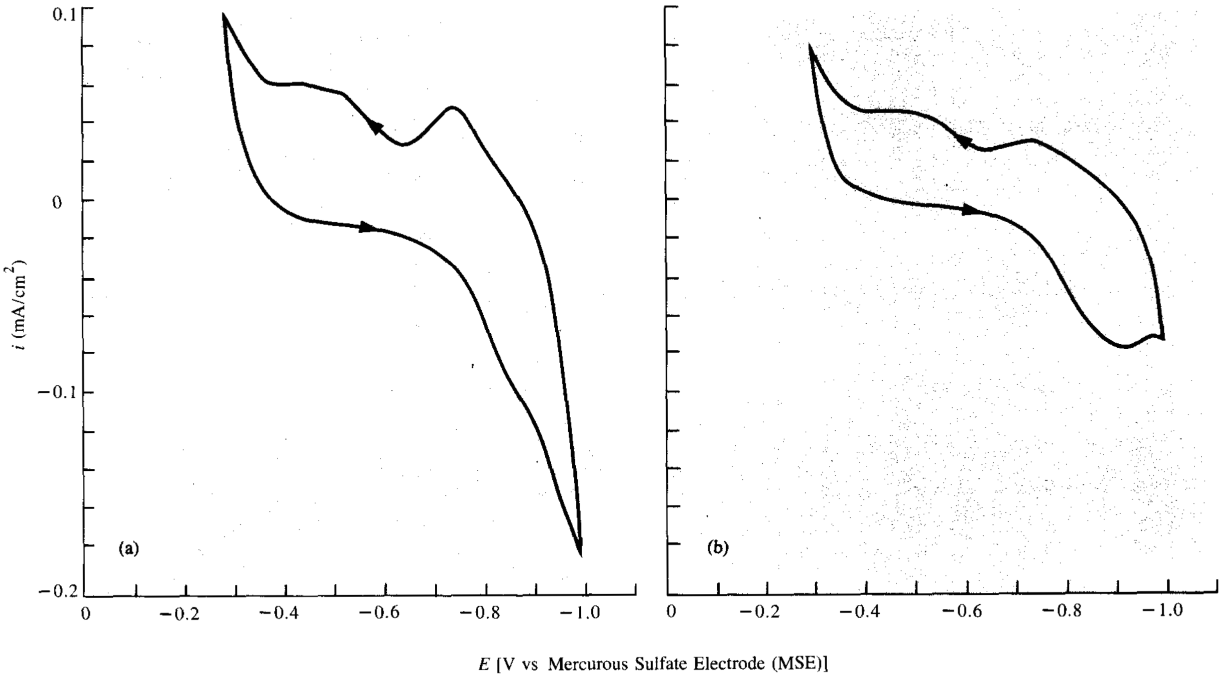

Figure 1

Cyclic voltammetry in 0.01 M $HClO_4$ of a Cu electrode (a) immersed in a Pd-Sn mixed colloid solution and (b) immersed in a Pd-Sn colloid known to have inferior catalytic activity. Sweep speed was 20 mV/s. (From Ref. [8]). Reprinted by permission of the Electrochemical Society, Inc.

Both Cu and epoxy substrates were used in the analytic studies of the acceleration process. After cleaning and identical activation procedures, the samples were immersed for one minute in the accelerator of interest. The accelerators studied were 1 M HCl, 1 M NaOH, 1 M NH_4BF_4, 1 M NH_4HF_2, 0.13 M EDTA at pH 11.7, and 0.13 M EDTA at pH 4.5.

The electron microprobe analyses were performed using an Applied Research Lab Scanning Electron Microprobe Quantometer; the data were analyzed according to the method of Reuter [18]. The characteristic X-ray Pd Lα and Sn Lα transitions were monitored simultaneously using wavelength dispersion spectroscopy. For epoxy substrates, ~10 nm of Al was evaporated on the sample before the analysis to prevent charging. The relative accuracy is at best ±10% and can be worse, depending on the counting statistics. The relative precision is a function of the statistics and for thicker colloid films is on the order of ±2% at the 95% confidence level.

Analyses were obtained at more than one point on most samples, and in most cases several nominally identical samples were also analyzed. The point-to-point variation across a sample was large, often exceeding the sample-to-sample variation. This variation is not caused by an inaccuracy in the technique; it is the result of the nonuniform coverage by the discrete colloid particles on the scale of the measurement.

The instrument used for the X-ray photoelectron spectroscopy (XPS) analysis was a Hewlett-Packard 5950B X-ray photoemission spectrometer with a crystal monochromator on the X-ray source, yielding 1486.6-eV Al Kα X-rays. The Sn 3*d*, O 1*s*, and Pd 3*d* binding energies were monitored, in addition to the Cu Auger peak. The XPS peak assignment was made using the Perkin-Elmer *Handbook of X-ray Photoelectron Spectroscopy.* The Sn(II) and Sn(IV) binding energies were not resolved, but information about the oxidation state of tin would be questionable in any case, since the samples were handled in air.

Results of the analyses

The information that can be gained about Pd-Sn catalysts using the cyclic voltammetric technique was discussed in detail in [8] and is illustrated in **Figure 1(a).** A Cu electrode was immersed in the Pd-Sn colloid and rinsed, depositing ~1 $\mu g/cm^2$ of Pd and 2-5 $\mu g/cm^2$ of tin. The cyclic voltammetry was performed in an inert electrolyte, i.e., one that is not strongly adsorbed and does not strongly attack the surface.

Copper itself does not undergo electrochemical reactions over the potential range shown in Fig. 1(a), except for some dissolution evidenced as a small, positive current near the positive limit of the potential sweep. Thus little background current is due to the Cu itself. The cause of the other observed currents has been established [8] by comparison with similar but simpler systems. A Cu electrode, after immersion in a $SnCl_2$ colloid, exhibits a pair of peaks: an oxidation peak at ~ −0.5 V in the positive-going (anodic) sweep and a reduction peak at ~ −0.8 V in the negative-going (cathodic) sweep. The currents at these potentials in Fig. 1(a) can thus be assigned to the oxidation of the Sn(II) in the adsorbed colloid to Sn(IV) and its subsequent reduction back to Sn(II). The adsorbed colloid is not completely stable on the surface, and cycling of the potential leads to slow changes in the curve. For consistency, this study always recorded the second sweep.

When a Cu electrode is immersed in a $PdCl_2$ solution, an exchange reaction results in the deposition of Pd metal on the surface. The Pd can adsorb and absorb H atoms, as evidenced by a large current in the cathodic sweep. When the sorbed H is desorbed during the anodic sweep, a current peak is observed. The potentials at which the sorption current and the desorption peak occur depend on the morphology of the Pd. When the process must overcome a higher energy barrier, it is shifted toward more negative potentials. The potential range of hydrogen sorption indicates [8] that the process is most favorable on pure bulk Pd, less favorable on finely divided Pd deposited on Cu by an exchange reaction, and least favorable on the metallic Pd in the Pd-Sn colloid. That is, the Pd in the colloid is less like bulk Pd than the exchange Pd deposit. The current negative to the tin shoulder at ~ −0.8 V in the cathodic sweep and the peak at ~ −0.75 V in the anodic sweep in Fig. 1(a) are due to the hydrogen sorption process in the Pd in the colloid.

The features of the curves in Fig. 1 can give a qualitative assessment of the activity of the Pd-Sn catalyst. The procedure of Osaka et al. [9], which somewhat resembles our method, is a quantitative measure of the amount of Pd and tin deposited on a surface. We have found, however, that colloids depositing equal amounts of Pd and tin can have quite different activities, and this distinction can be made using our technique.

A curve characteristic of a less active catalyst [8] is given in **Figure 1(b).** This particular colloid was prepared with half the HCl concentration of that in Fig. 1(a). The resulting solution was not sufficiently acidic to maintain stannic ions in solution; Sn(IV) formed during synthesis of the colloid or during its use could precipitate on the colloid particles and bury the active Pd core. As a result, the Pd was inaccessible for the H-sorption reaction, and the cathodic current and the anodic peak were consequently reduced in magnitude. For inferior catalysts, the Cu dissolution signal is usually small, since the Cu is also uniformly covered by tin species. Palladium that is inaccessible for H sorption is also inaccessible as a catalyst for HCHO oxidation during electroless Cu plating. The magnitude of the H-desorption peak at ~ −0.75 V in the cathodic sweep is a measure of the activity of the colloidal catalyst.

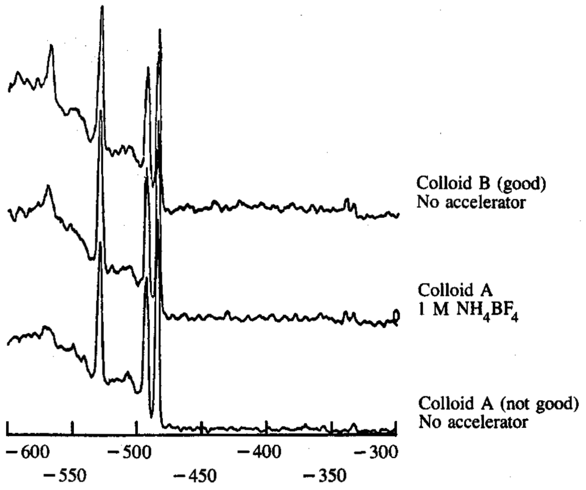

Figure 2

XPS spectra for three activated Cu surfaces. Top: activation using a catalyst shown electrochemically to have good catalytic behavior; bottom: activation using a catalyst shown electrochemically not to have good catalytic behavior; center: same catalyst as at bottom, but followed by NH_4BF_4. (From Ref. [8]). Reprinted by permission of the Electrochemical Society, Inc.

XPS studies have corroborated the conclusions of the electrochemical measurements [8]. XPS spectra of Pd-Sn catalysts that the cyclic voltammetry had indicated were good (i.e., exhibited a large H-desorption peak) and bad (i.e., exhibited a small peak) are shown in **Figure 2.** Colloid A had been in use some time, and an effort had been made to raise its pH. This procedure would result in the precipitation of Sn(IV) oxides and hydroxides. Colloid B was freshly prepared. The peaks in Fig. 2 are assigned as follows: the 570-eV peak is a Cu Auger peak; the 530-eV peak is due to oxygen; the doublet at ~490 eV is due to tin; the small doublet at ~330 eV is due to Pd.

For the inferior catalyst A (at the bottom), the main signals are those from tin and oxygen. The Cu Auger signal is indistinct and there is no significant Pd signal. An electron microprobe analysis of these samples gave Pd coverages of 0.6 ± 0.1 $\mu g/cm^2$ for colloid A and 1.0 ± 0.1 $\mu g/cm^2$ for colloid B, and tin coverages of 2.0 ± 0.3 $\mu g/cm^2$ for A and 1.9 ± 0.1 $\mu g/cm^2$ for B (i.e., the differences in coverage are small). Yet XPS shows that the Pd of colloid A is buried by a layer of tin salts at least 3 nm thick (the XPS sampling depth). When the tin is removed with an NH_4BF_4 accelerator (middle spectrum), both the Cu and Pd signals become more

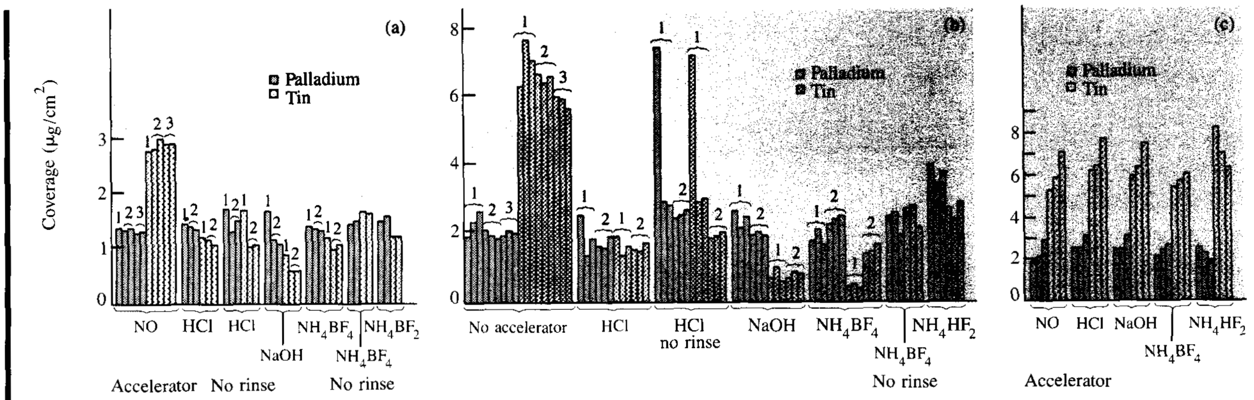

Figure 3

Electron microprobe results showing the effect of various accelerators on Pd and Sn coverage (a) on activated Cu surfaces; (b) on activated epoxy surfaces; and (c) on activated epoxy surfaces that had been heated between the activation and acceleration steps. (From Ref. [8]). Reprinted by permission of the Electrochemical Society, Inc.

pronounced. The conclusions agree well with those from the electrochemical measurements, which showed inaccessible Pd and very little exposed Cu for colloid A.

The differences between good and bad catalysts cannot be unambiguously distinguished by techniques like electron microprobe (EMP) analysis. In conjunction with other methods, however, EMP gives useful information about the activation process. The effects of accelerators can be illustrated by EMP data, as shown in **Figures 3(a)** and **3(b).** In these figures, analyses made on different spots of the same sample are grouped together with brackets; different samples are labeled by numbers.

Figures 3(a) and 3(b) show the effects of various accelerating solutions on the Pd and Sn coverages on Cu and epoxy substrates. The activation process deposits more Pd-Sn colloid on the epoxy than on the Cu. On unaccelerated samples, the tin coverage is larger than the Pd coverage (whether the coverages are measured in weight or number of atoms of the deposited material). Acceleration removes about half to two-thirds of the tin from Cu surfaces and more than two-thirds of the tin from epoxy surfaces. There is little change in the Pd coverage after acceleration.

The effect of rinsing between the activation and acceleration steps was investigated. Pure water, with a pH near 7, is an extremely poor solvent for tin salts. Stannic and stannous hydroxides and oxides can form during the rinse step; it was not known whether the removal of the tin becomes more difficult after formation of these species. The effect of the rinse was investigated with HCl and NH_4BF_4 accelerators, as shown in Figs. 3(a) and 3(b). The tin coverage after rinsing and acceleration was always at least as low as that after acceleration with no rinse, showing that the rinsing step is not detrimental.

The effect of drying the sample between activation and acceleration was also investigated. **Figure 3(c)** gives results for activated epoxy surfaces that were dried before the acceleration step. If the sample is dried after activation, acceleration does not remove any significant amount of Sn. Similar results were obtained on Cu substrates. During drying, SnO_2 can form; this compound is very insoluble and is difficult to remove. Thus, if the processing requires drying of the sample (before photolithography, for example), the drying should be done after the acceleration step.

The cyclic voltammetry in Pd-Sn colloids is changed by acceleration. Different accelerators have quite different effects on the curves. One example is given in **Figure 4.** The salts of EDTA (ethylenediamine tetra-acetic acid) are strong complexants for tin ions and should be effective in removing tin from the surface. Indeed, EMP analyses show that EDTA is comparable to the other accelerators studied. After immersion of activated Cu in EDTA, the cyclic voltammetry of the sample in dilute $HClO_4$ shows a much larger H-sorption current and a higher H-desorption peak. In other words, the Pd in the colloid appears to be more accessible for the H-sorption reaction. This increased accessibility of the Pd should also improve its catalytic activity for the electroless Cu reaction.

On the basis of the results of Fig. 4 we further investigated EDTA. It was found to be an effective accelerator. It has the advantage of being useful over a wide pH range, allowing one to avoid the extremes in pH characteristic of many other accelerators.

Conclusions

New understanding of Pd-Sn colloidal catalysts and of the process of activation for electroless Cu plating has been gained through the use of electrochemical and surface analytic techniques. The effectiveness of the Pd-Sn activator was found not to be simply related to the Pd coverage; it was also determined by the morphology of the colloid particle.

A thick layer of ionic Sn surrounding the active tin in the colloid core makes the Pd inaccessible as a catalyst for electroless Cu deposition.

An electrochemical technique has been developed to assess the activity of Pd-Sn catalysts. The method depends on the ability of Pd to adsorb and absorb hydrogen. Palladium that is not accessible as a catalyst for Cu deposition is also inaccessible for H sorption. The H-desorption peak in the cyclic voltammetry of colloid-covered Cu surfaces in $HClO_4$ can be used as a qualitative measure of the catalytic activity of the Pd-Sn colloid. The conclusions of the electrochemical study have been confirmed by XPS and by functional tests.

The process of acceleration, i.e., the removal of excess ionic tin from the colloid-covered surface, has also been studied. If acceleration takes place directly after the activation procedure, all of the accelerators studied are effective in removing tin while leaving a large quantity of the Pd on the surface. The effect of rinsing between the activation and acceleration steps was investigated; the rinse step was not found to be detrimental. If the surface is dried after the activation, the tin salts form SnO_2 on the surface, and none of the accelerators removes Sn from the dried surface.

Electron microprobe analysis shows little difference between the accelerators studied, but the accelerators have varied effects on the cyclic voltammetric analysis. On the basis of the electrochemical measurements, EDTA was shown to be a potentially very effective accelerator. This conclusion was subsequently borne out by functional tests.

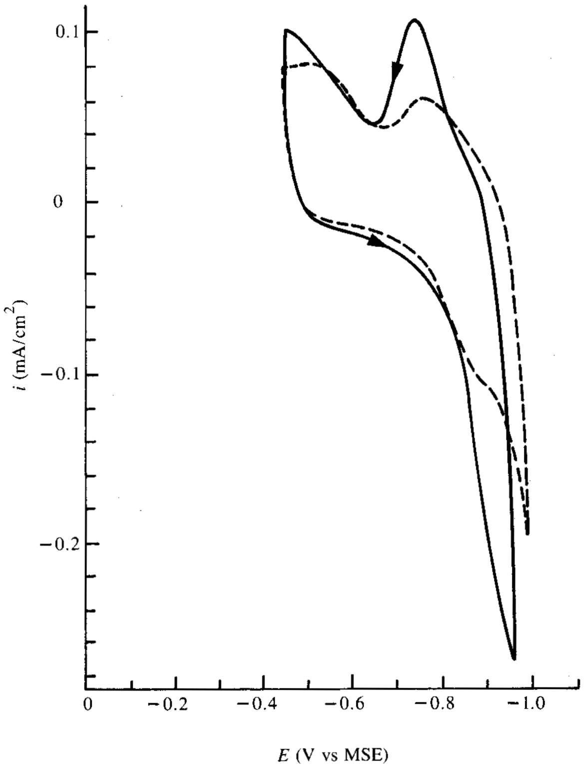

Figure 4

Similar to Fig. 1, with no accelerator (dashed line) and after acceleration with 0.13 M solution of EDTA at pH 12.

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References

1. G. P. Power and I. M. Ritchie, "Mixed Potential Measurements in the Elucidation of Corrosion Mechanisms, Part 1," *Electrochim. Acta* **26,** 1073–1078 (1981).
2. G. P. Power, W. P. Staunton, and I. M. Ritchie, "Mixed Potential Measurements in the Elucidation of Corrosion Mechanisms, Part 2," *Electrochim. Acta* **27,** 165–169 (1982).
3. A. Molenaar, M. F. E. Holdrinet, and L. K. H. vanBeek, "Kinetics of Electroless Cu Plating with EDTA as the Complexing Agent for Cupric Ions," *Plating* **61,** 238–242 (March 1974); P. Bindra and J. Tweedie, "Mechanisms of Electroless Metal Plating. I. Application of Mixed Potential Theory," *J. Electrochem. Soc.* **130,** 1112–1114 (1983).
4. Perminder Bindra, David Light, and David Rath, "Mechanisms of Electroless Metal Plating: I. Mixed Potential Theory and the Interdependence of Partial Reactions," *IBM J. Res. Develop.* **28,** 668–678 (1984, this issue).
5. R. L. Cohen, J. F. D'Amico, and K. W. West, "Moessbauer Study of Tin(II) Sensitizer Deposits on Kapton," *J. Electrochem. Soc.* **118,** 2042–2046 (1971); R. L. Cohen and K. W. West, "Solution Chemistry and Colloid Formation in the Chloride Sensitizing Process," *J. Electrochem. Soc.* **119,** 433–438 (1972).
6. R. L. Cohen and K. W. West, "Generative and Stabilizing Processes in Sn-Pd Sols and Pd Sol Sensitizers," *J. Electrochem. Soc.* **120,** 502–508 (1973).
7. R. L. Cohen, R. L. Meek, and K. W. West, "Sensitization with Pd-Sn Colloids I. Role of Rinse and Accelerator Steps," *Plating* **63,** 52–55 (May 1976); R. L. Meek, "A Rutherford Scattering Study of Catalyst Systems for Electroless Cu Plating," *J. Electrochem. Soc.* **122,** 1177–1185 (1975); T. Osaka, H. Nagasaka, and F. Goto, "Effects of Activation and Acceleration on Co-P Thin Films," *J. Electrochem. Soc.* **128,** 1686–1691 (1981); J. J. Grunwald, S. Gottesfeld, and D. Laser, "An Auger Spectroscopic Study of the Catalysis Process for Electroless Cu Plating," *Plating* **68,** 71–74 (October 1981).
8. J. Horkans, "A Cyclic Voltammetric Study of Pd-Sn Colloidal Catalysts for Electroless Deposition," *J. Electrochem. Soc.* **130,** 311–317 (1983).
9. T. Osaka, H. Takematsu, and K. Nihei, "A Study on Activation and Acceleration by Mixed Palladium Chloride/Tin Catalysts for Electroless Cu Deposition," *J. Electrochem. Soc.* **127,** 1021–1029 (1980); T. Osaka, H. Nagasaka, and F. Goto, "An Electron Diffraction Study on Mixed Palladium Dichloride/Tin Dichloride Catalysts for Electroless Plating," *J. Electrochem. Soc.* **127,** 2343–2346 (1980).
10. E. B. Saubestre, in *Modern Electroplating,* F. A. Lowenheim, Ed., John Wiley & Sons, Inc., New York, 1974, p. 636.

11. K. Wiebusch, "Influence of Moulding Conditions and Pretreatment on Properties of ABS Plastics," *Prod. Finishing (Lond.)* **19,** 44–52 (November 1966).
12. W. Riedel, "Investigations into Relieving Processes in Electrodeposited Cu," *Galvanotech.* **59,** 167 (1968).
13. D. H. Kaeble, *J. Adhesion* **1,** 102 (1969).
14. E. B. Saubestre et al., "The Adhesion of Electrodeposits to Plastics," *Plating* **52,** 982–1000 (1965).
15. A. Rantell, "The Influence of Surface Chemistry on Adhesion of Cu Deposits on Plastic Substrates," *Trans. Inst. Metal Finishing* **17,** 197–202 (1969).
16. K. Wiebusch, H. Ebneth, and K. Kato, *Polymer* **9,** 417 (1968).
17. R. J. Zeblisky, U. S. Patents 3,672,938 (1972) and 3,672,671 (1972).
18. W. Reuter, "The Ionization Function and its Application to the Electron Probe Analysis of Thin Films," *Proceedings of the 6th International Conference on X-Ray Optics and Microanalysis*, G. Shinoda, K. Kohra, and T. Ichinokawa, Eds., University of Tokyo Press, Tokyo, 1972.

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